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THE CATHODE-RAY OSCILLOGRAPH AND ITS APPLICATION TO THE EXACT MEASUREMENT OF EXPLOSION PRESSURES, POTENTIAL CHANGES IN VACUUM TUBES AND HIGH TENSION MAGNETOS.*

BY

DAVID A. KEYS, Ph.D.

Department of Physics, McGill University, Montreal.

1. INTRODUCTION.

IN MANY physical and engineering problems it is necessary to possess an instrument which will record accurately very rapid variations in electrical potential. For such a purpose any device possessing a recording system with appreciable mass would not be suitable owing to the inertia of its moving parts. The ordinary Braun tube, in which a beam of electrons passes between two deflecting charged plates and falls on a fluorescent screen, is satisfactory for those cases in which the electrical variations are periodic and go through the same cycle many times. The beam of cathode rays will traverse the same path each cycle, and the fluorescent curve traced on the screen may be photographed with an ordinary camera, and a permanent record thus obtained. A very useful and improved type of such an instrument has recently been described by J. B. Johnson.[1] But in other cases, where the

* Presented at the Stated Meeting of The Franklin Institute held Wednesday, April 18, 1923.

[1] *Journ. Opt. Soc. of America*, 6, p. 701 (1922).

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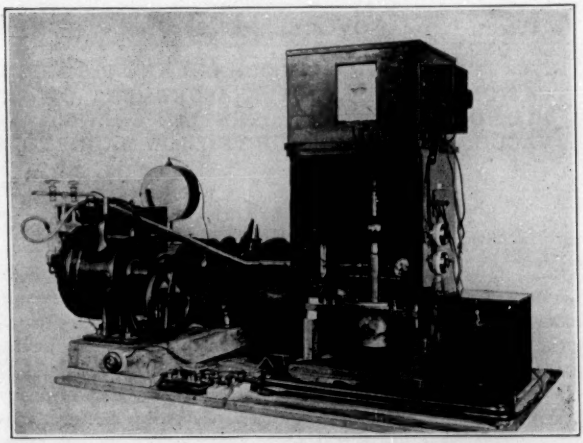
change is not periodic but impulsive, some other form must be used, as the fluorescent light caused by a single transit of the spot across the screen would fail to leave any impression when photographed as above.

The present paper contains an account of a recent form of oscillograph which was devised by Sir Joseph Thomson and used by the writer. With this instrument impulsive changes in potential

FIG. 1.



Wood's oscillograph.

occurring in less than one ten-thousandth of a second may be measured. By employing the piezo-electric properties of tourmaline, the apparatus has been adapted to measure the time-pressure changes which take place when a gaseous mixture is exploded in a closed vessel similar to the cylinder of an internal combustion engine. The tourmaline crystals transform the pressure variations into alterations in electrical potential.[2] The same arrangement has been used to investigate the nature of the pressure waves produced in water by the detonation of charges of gun-cotton and T.N.T. under the water. This is the only method

[2] *Phil. Mag.*, **42**, p. 473 (1921).

which will give a continuous and accurate time record of such pressure changes, the recording system possessing practically no inertia. In this type of cathode-ray oscillograph, the photographic plate is placed inside the vacuum tube in front of the fluorescent screen so that the cathode rays impinge directly on the plate and affect it in a single transit. When the plate is removed and developed, a permanent record is obtained. In the Dufour [3] oscillograph, the cathode rays also fall directly on a photographic

FIG. 2.

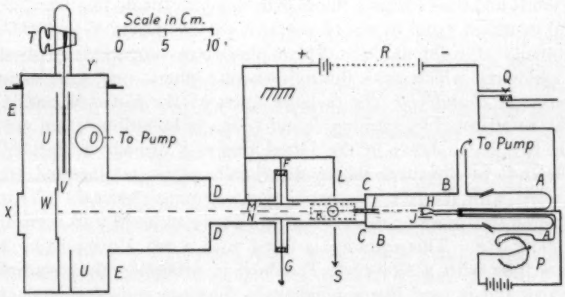


Diagram of oscillograph.

plate, but owing to the larger velocity of the electrons and the method of recording the time intervals, the tube is not very sensitive and is unsuitable for many purposes. Recently A. B. Wood [4] has described a more robust type of oscillograph (Fig. 1), essentially the same as that previously used by the writer, though differing in some minor details which will be mentioned later.

2. THE OSCILLOGRAPH.

The most recent form of cathode-ray oscillograph used by the writer is shown diagrammatically in Fig. 2, which is drawn to scale. It consists of a ground-glass stopper *AA* which fits into the glass tube *BB*. Two wires are sealed through the stopper as shown and carry at their extremity a small brass cylinder, in the centre of which is a helix *J*, consisting of four or five turns of fine tungsten wire. The other ends of the wire are connected

[3] *Journ. de Physique et le Radium*, 1, p. 147 (1920).
[4] *Proc. Lond. Phys. Soc.*, 35, p. 109 (1923).

to an eight-volt storage battery and variable resistance P supported on an insulating stand. By means of this battery and resistance, the tungsten wire J may be heated to any desired temperature. The arrangement is similar to the cathode in an ordinary Coolidge X-ray tube. The glass tube BB is fastened with litharge and glycerine cement to a brass tube CD. This tube is closed at the end CC by a brass plate through the centre of which passes a fine tube I about ¼ mm. in diameter. The surface of the plate CC, facing the filament J, is coated with willemite crystals and thus forms a fluorescent screen. Inside the tube CD, and insulated from it, are two sets of parallel plates K and MN, mutually at right angles. These plates are supported by stout brass wires which pass through ebonite plugs, one pair being shown at F and G. The distance apart of the plates M and N may be adjusted by pushing F and G in, or by pulling them out. The two plates shown by the dotted lines at K are also adjustable. The ends of the tubes where the ebonite plugs are inserted are covered with Everett wax, making a vacuum-tight seal. CD is soldered into a wider tube, which in turn is attached to a vertical cylinder EE. This cylinder is fitted with a top Y supporting a glass tube with a stop-cock T, which is ground with a central groove and is used like a windlass.[5] The top end of this glass tube is sealed. In the centre of the tube EE is a rectangular box UU in which a holder slides, carrying a photographic plate V, the holder being attached by a thread to the cock T, so that it may be raised or lowered by turning the tap. The sensitive side of the photographic plate V faces the tube CD. W is a willemite screen which may be viewed through the glass window X in the side of the cylinder EE as shown. The cover Y fits tightly the top of the cylinder EE and a little wax makes the joint vacuum tight. The whole apparatus is evacuated by means of a "Hi-vac" vacuum pump to 10^{-3} mm. of mercury pressure, through two tubes, one shown at O and the other attached to B.

One of each pair of deflecting plates ML and K is connected to earth as well as the brass part CDE. R is an Evershed and Vignoles 6000-volt, 15-milliampere, D. C. generator, the positive terminal of which is earthed and the negative terminal is connected through the key Q with the filament J. When the filament

[5] See "Rays of Positive Electricity," by Sir Joseph Thomson, 2nd edition, p. 32.

is heated by the battery and the key Q depressed, the strong electrostatic field between J and CC accelerated the electrons emitted by the hot filament towards the plate CC. The cylinder H concentrates the rays along its axis and by observing the willemite screen on CC, one can readily see where the stream is striking. By turning the stopper AA and using an external bar magnet when necessary, part of the beam may be directed through the opening I. The electrons pass between the two pairs of deflecting plates and fall on the screen W, causing a bright green spot. The leads G and S are also temporarily connected to earth while these adjustments are made.

The quality of the spot obtained on the screen W is very important and the successful working of the apparatus depends upon getting this sufficiently bright and small. It was found in the early work with the oscillograph, that the helix in H is the best form of filament and also that the presence of some gas in the tube B as well as the cylinder H helps to concentrate the electrons in a small beam. By judiciously adjusting the temperature of the filament J and the potential of the generator R, it was found that very bright and tiny spots could be obtained on the screen W. The fine spots were much smaller than the optical image of the opening I and produced clear thin lines on the photographic plate, if displaced rapidly across it.

The plate S is attached to the source of potential, the variation of which is to be investigated, such as the insulated pole of a magneto, the exploring electrode in a vacuum tube or the insulated plate of the tourmaline pressure detector to be described later. Any difference in potential between L and S will cause the spot to move in a direction perpendicular to the plane of the paper. The plate G is attached to a Vreeland oscillator, the other terminal of which is connected to earth. This produces a pure sinusoidal alternating e.m.f. between the plates M and N, the period of which may be altered to any desired value by changing the capacity in the usual way.[6] This alternating electrostatic field between M and N produces a vertical displacement of the spot, which will trace out on the screen W a line which is at right angles to the motion caused by the field between the other pair of plates at K. The Vreeland oscillator thus produces the

[6] *Phys. Rev.*, 27, p. 286 (1908).

time axis of the oscillograph and since the power consumption is very small, there will be no distortion of the wave form, with the result that the spot will travel up and down with simple harmonic motion. The time taken for it to reach any point in its path from either end is readily obtained when the frequency is known, by the usual simple transformation.

In the earlier type of apparatus used,[7] a time displacement was produced by a magnetic field produced by an alternating current. This field was parallel to the plates K, but the second pair of plates M and N were not used. Owing to the presence of harmonics in such an alternating current, the vertical motion of the spot was not strictly simple-harmonic, and this fact introduced slight errors in the time scale. Doctor Wood overcomes this difficulty by using the time constant of an electromagnet to give a displacement across his plate. This method has the advantage that the time scale is practically uniform, if proper precautions are taken. If the oscillograph is to be used for impulsive measurements, this method will involve additional mechanical contact arrangements and would be impracticable in cases when the exact time at which the impulsive action takes place cannot be predetermined to within a second.

In the operation of the oscillograph, the screen W is viewed through the window X and all adjustments made until the spot and vertical time line are satisfactory. The key Q is then opened, and the photographic plate V lowered in front of W and thus exposed to the direct action of the electrons. The actual light from the filament, which comes through I is not sufficient to affect the plate appreciably. The key Q is so constructed that on depressing it, connection is first made to the generator R, thus producing the cathode-ray beam in the oscillograph. On further depressing the key, a contact is made which results in a change in potential of the plate at K, caused by the phenomenon under investigation. During the interval between the closing of these two circuits, the spot travels several times up and down, producing a vertical zero line on the plate. The horizontal displacement of the spot is proportional to the potential difference between the two plates at K, and so a time-potential curve is obtained on the photographic plate. The key

[7] Glazebrook, "Dictionary of Applied Physics," 1, p. 76.

Q is now released, air admitted into the apparatus and the plate removed for development. The type of curve obtained will naturally depend upon the nature of the phenomena investigated. To reduce the tracing on the plate to a uniform time scale, the coördinates of points on the curve must be obtained. This is done by placing the plate in a holder similar to that used by Sir Joseph Thomson and the coördinates of the points read.[8] The time-displacement curve may then be plotted on a uniform scale.

3. APPLICATION OF THE OSCILLOGRAPH TO THE MEASUREMENT OF IMPULSIVE PRESSURES.

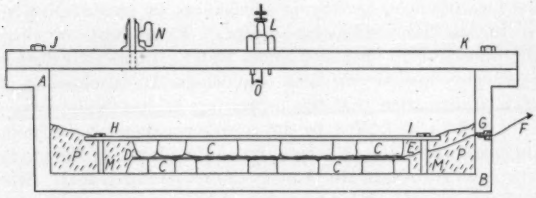
One of the chief applications of this form of oscillograph is to the measurement of very rapid changes in pressure, such as occur in internal combustion engines, or in guns, or in the neighborhood of an explosion under water. In investigating the time-pressure history of such explosions, it is essential for accurate information that the measuring device should have as little inertia as possible. In any crusher gauge or mechanical arrangement there will be errors due to the inertia of the moving system, especially when the changes in pressure are rapid. Moreover, the devices which have been used previously in such investigations will not record large negative changes in pressure—they give $\int Pdt$ over short-time intervals and the values of the blocks of momentum vary according to the instrument used. There is a practical limit to the smallness of the time intervals which may be used and so what is usually measured is a series of integrals and not the true pressure-time curve. Sir Joseph Thomson suggested the use of crystals possessing the piezo-electric properties such as tourmaline or quartz, for transforming the pressure waves into corresponding variations in electrical charge. These electrical charges can then be registered on the oscillograph and a true time-pressure curve obtained.

The final type of crystal detector developed for measuring the changes of pressure in gaseous and under water explosions is shown in Fig. 3. It consists of a brass cylinder AB provided with a metal lid JK which may be screwed down with a number of bolts. This box contains two layers of tourmaline crystals CC with a lead plate ED between them. Tourmaline

[8] "Rays of Positive Electricity," 2nd edition, p. 35.

crystals were used in preference to quartz because the charge produced on the opposite faces of the crystals is directly proportional to the hydrostatic pressure to which the crystals are subjected, whereas in the case of quartz, a lateral pressure produces a charge of opposite sign to that produced by a transverse pressure, a hydrostatic pressure thus producing no appreciable resultant charge. The crystals are mounted in two layers so that all the positive faces of the lower layer are in contact with *DE* and the positive faces of those in the upper layer are downwards, *i.e.*, also in contact with the lead plate. A thin sheet of steel *HI*, fitted with screws *MM*, clamps these crystals down

FIG. 3.



Piezo-crystal detector.

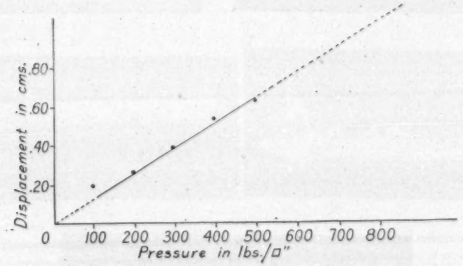
tightly, so that they are held in place and also under pressure against the plate *DE*, which is connected by an insulated wire *F*, passing through the plug *G*, to the insulated plate *S* of the oscillograph. The space *PP* is filled up with vaseline to keep the plate *DE* insulated. The brass cylinder is connected to earth.

Since the crystals are under pressure due to the bolts *MM*, any lessening of the pressure in the region above *HI* will cause a charge on the plate *DE*, which will be of opposite sign to that produced by an increase in pressure on *HI*. Thus it is evident that the arrangement will register negative as well as positive pressures. This is an important advantage which this device has over previous types of gauges. Moreover, since the pressure wave has only to pass to the crystal in order to produce the electrical separation, *i.e.*, the charge on the plate *DE*, no bodily motion of the crystals or any other part of the apparatus is necessary.

To use this detector for studying the time-pressure changes

in explosions, the vessel must be calibrated. This is done by placing the vessel in the position in which it is to be used in the investigation and connecting the wire F to the oscillograph. The lid JK is bolted down and the pot is completely filled with gasolene or some other liquid which is not a very good electrical conductor. A static pressure is applied to the liquid in the vessel by means of an oil pump attached to the tap N. The resulting pressure in the vessel produces a corresponding charge on the plate DE. This charge raises the potential of the plate of the oscillograph and the cathode beam is accordingly deflected. The amount of this deflection is found to be directly proportional to the pressure applied to the crystals. The pressures are read from a gauge attached to the pump and the deflections measured on the photographic plate of the oscillograph. The vessel is thus calibrated *in situ* and therefore no corrections are necessary for capacity as this is not altered during an investigation. If a pressure is applied to the crystal detector and the wire F momentarily earthed so as to remove the charge caused by the increase in pressure, then on releasing this pressure, there will be a deflection of the cathode-ray beam in a direction opposite to that caused when a pressure is applied. The charge produced on the release of the pressure equals that caused by the application of the pressure, but is of opposite sign. Since a pressure may be released more rapidly than applied, the vessels were usually calibrated by releasing the pressures. A typical calibration curve obtained in this way is shown in Fig. 4.

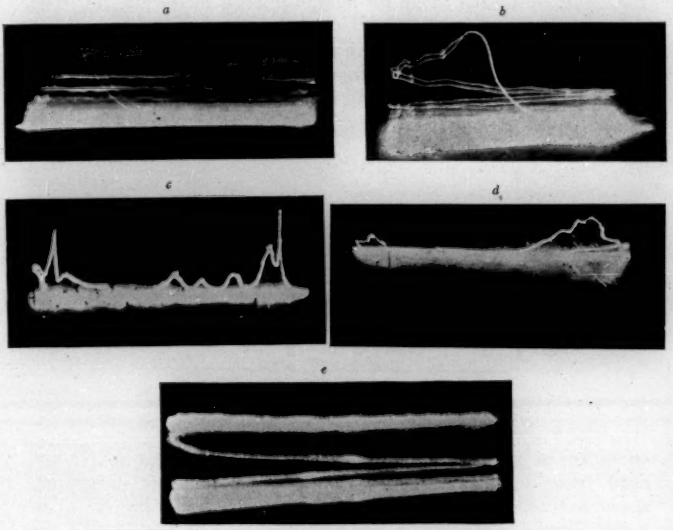
FIG. 4.



Calibration curve of piezo-crystal detector.

The calibrated vessel may now be used to investigate the time-pressure history of gaseous explosions. When used for such purposes, an ordinary automobile spark plug L is fitted into the lid (Fig. 3) and the sparking points are joined by a thin wire O. This wire is connected with a battery through the

FIG. 5.



Examples of photographic records obtained.

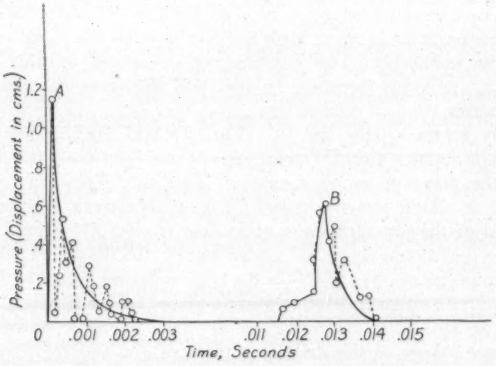
(*a*) and (*b*) Explosion of mixture of electrolytic gas and air.
(*c*) Explosion of guncotton under water showing echo also.
(*d*) Explosion of T.N.T. under water, showing echo also.
(*e*) Time of adjustment of potential in a Geissler tube.

N. B. Plates *a* to *d* had to be touched up in places with Chinese white for reproduction purposes, but *e* is untouched.

second contact of the key Q (Fig. 2). The vessel is exhausted through the tap N and the explosive mixture introduced. The oscillograph is then adjusted, the photographic plate lowered into position and the key Q depressed. Before the gas is detonated the cathode-ray beam will execute several vertical oscillations in its zero position and a zero line is thus traced

on the plate. When the explosion takes place, by the heating of the wire *O*, the beam will be deflected horizontally, and the combination of the two motions gives the time-pressure record. Fig. 5 is a reproduction of some curves obtained in photographic plates in this way. It frequently happens that there are two tracing spots very close together and in such cases each spot traces out its own path. Either of these paths may be measured up for plotting the time-pressure curve on a uniform time scale. In

FIG. 6.



Explosion of guncotton.

Fig. 6 are given the time-pressure curves for three different mixtures of electrolytic gas and air, obtained with this apparatus. It is apparent from these results that the scheme has an important application in the study of the detonation of various mixtures of oils and vapors for use in internal combustion engines. Moreover, by placing crystals in the piston of a gasolene engine, or in any desired part of the walls, the internal ballistics of the engine may be studied. With the continual growth in the use of internal combustion engines, it is necessary that they should be operated with the greatest economy. The piezo-electric method described above places an instrument in the hands of an engineer with which he may determine the most efficient and economical explosive mixtures for use in such engines.

The application of the piezo-electric method of measuring explosion pressures in guns is at once apparent. J. C. Karcher [9] has recently used the piezo-electric properties of quartz in conjunction with a ballistic *galvanometer* for such a purpose. The use of the galvanometer has the disadvantage that in cases where the initial and final pressures are the same, and the pressure changes take place very rapidly, the resulting charge passing through the galvanometer is zero and no deflection will result. By substituting the cathode-ray oscillograph for the galvanometer, the method would be practical in all cases.

The apparatus may also be used for the determination of the specific heats of gases at high temperatures by the usual constant volume method.[10] The outstanding advantage of this device, over all previous methods, is, that the apparatus has practically no inertia.

By removing the lid *JK* (Fig. 3) and placing the crystal detector under water, the arrangement has been used for measuring the pressure waves resulting from the explosion of small mines in water near the vessel. Fig. 6 represents a typical time record of the pressure wave at 12 feet from a 2¼-pound charge of dry guncotton detonated under water. In the figure, *A* represents the direct wave and *B* is the echo reflected from the bottom. By having two such detector vessels placed in the water at a fixed distance apart and arranging the crystals in one so as to give a positive charge to the deflecting plate of the oscillograph, while the other produces a negative charge on the same deflecting plate, due to the pressure wave, the velocity of propagation of the wave has been determined. The average of a number of observations, taken in this manner, gave a velocity of approximately 5100 feet a second, a value slightly in excess of the velocity of sound. Such experiments will also show the change in the form of the wave with distance from the source.

The experiments described above will give a general idea of the wide and varied application which this method offers for the measurement of impulsive pressures. By inserting suitably mounted crystals of quartz or tourmaline in the struts and frame rods of aeroplanes, the rapid variations in both tensions and compressions in these members may be investigated when the aero-

[9] Bureau of Standards, Scient. Papers, **18**, p. 257 (1922).
[10] M. Pier, *Zeitschr. f. Elektrochemie*, **16**, p. 897 (1910).

plane is in actual flight. This would necessitate an alteration in the cathode-ray tube so that it would be more compact, but that could be accomplished by suitable design.

4. THE MEASUREMENT OF RAPID CHANGES IN ELECTRICAL POTENTIAL.

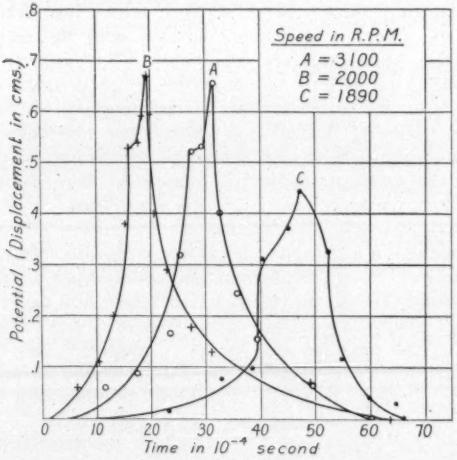
Besides the use of the Thomson cathode-ray oscillograph for the measurement of pressures, the instrument has an important application to the investigation of electrical oscillations, both periodic and impulsive. Wood's paper, which has already been referred to, gives some results obtained with the oscillograph in measuring high-frequency oscillations. The instrument may also be used to measure the nature of the electrical surges on transmission wires, the characteristics of the magneto discharge, the nature of lightning flashes and many other phenomena of an impulsive nature of short duration. As illustrations of the application of the oscillograph in this connection, two investigations performed by the writer will be briefly mentioned.

The experimental investigation of the theory of the high-tension magneto is a matter of great importance to the automobile manufacturer. It is well known that some types of magnetos are much more efficient and reliable than others and the reason for this is not always apparent. Prof. Taylor Jones [11] has given a theory of the magneto and Dr. N. Campbell [12] has described some experiments investigating the characteristics of such magnetos. The method adopted by Campbell for measuring the time-potential curves in the magneto was ingenious, but a separate adjustment and experiment was necessary for determining each point on his curve. The *continuous* time-potential curve may, however, be easily obtained in a single exposure with the oscillograph. To do this, the plates L and S of the oscillograph (Fig. 2) are connected in parallel across the spark gap of the magneto. The magneto was driven by a motor, and while it was running discharges occurred between the usual points of the spark plug. The insulated pole of the plug was connected to the plate S of the oscillograph. The difference of potential between the plates S and L will vary with the potential difference between the points of the spark plug. By depressing the key Q for an instant, the cathode rays pass from the filament and a time

[11] *Phil. Mag.*, [6], **36**, p. 145 (1918).
[12] *Phil. Mag.*, [6], **37**, pp. 284, 372 (1919).

record is obtained on the photographic plate of the potential variations. In some cases two sparks occurred while the key Q was depressed and two curves were found upon the plate. Both tracings were found to give identical curves within the limit of error of the oscillograph. In Fig. 7 are given the time-potential curves for three different speeds of the magneto. The results

FIG. 7.



Magneto potential curves.

are in general agreement with those found by Doctor Campbell. In this way, the effect of changing the windings, shape and construction of the various parts of a magneto may be investigated with the object of obtaining the optimum arrangement for maximum efficiency.

Another interesting investigation, which this oscillograph made possible, is the determination of the time required for the initial discharge in a Geissler tube to reach its equilibrium state. The investigation was suggested to the writer by Sir Joseph Thomson and the results showed that the time required to establish the final distribution of potential along the tube depended

upon the nature of the gas in the tube.[13] An insulated electrode, which could be moved in the vacuum tube to any point between the main two electrodes, was connected to the insulated plate of the oscillograph, the cathode of the discharge tube being connected to earth. As the potential rose in the neighborhood of the exploring electrode, the beam was deflected and the time required for equilibrium to be established was thus determined. Changes in potential of a few volts which took place in a one hundred-thousandth of a second were measured with this device. In the case of air, the times required for the discharge to reach a steady condition varied from 1 to 80 ten-thousandths of a second.

5. CONCLUSION.

The type of cathode-ray oscillograph described in this paper supplies an instrument which has long been wanted in many investigations. In its robust form it will be useful to the engineer for the measurement of very rapid potential or pressure changes of an impulsive nature. The few experiments described above will, in a general way, indicate some of the various applications and possibilities of the method. This oscillograph has made it possible to measure changes in pressure or potential which occur in a hundred-thousandth of a second or less. New avenues of research are consequently opened for investigation which should result in practical results of great economic and commercial value.

The writer wishes to acknowledge his indebtedness to Sir Joseph Thomson for entrusting to him the development of this apparatus and also for his continual advice and encouragement during the investigations described. He also wishes to thank Dr. A. S. Eve for his helpful suggestions in the writing of this paper.

Lightning and Fires. (Clip Sheet, U. S. Department of Agriculture, No. 276.)—The annual destruction due to lightning fires in the United States is estimated to be as much as $20,000,000. In one State alone, Iowa, during the four years ending with 1922, the loss as given by the State fire marshal was $1,363,704, of which 61 per cent. was due to fires in farm barns. Very nearly all of such loss is preventable by proper rodding, says the Weather Bureau of the United States Department of Agriculture, in commenting on this tremendous loss.

[13] Thesis submitted for Ph.D. degree at Cambridge University, 1922.

Some Observations on Alpha Particle Tracks in a Magnetic Field. P. KAPITZKA. (*Proc. Cam. Phil. Soc.*, Lent Term, 1923.)—When an alpha particle passes through a gas, it breaks up some of the atoms in its path. C. T. R. Wilson decades ago showed how to make the path of the particle visible by rapidly expanding the gas and thus letting the atomic fragments serve as nuclei for the condensation of the water vapor present. This method has provided much information on the nature of the collisions of the particle with the atoms in its way. "In the recent experiments of Blackett, it was shown that by studying the forks and the kinks which occasionally occur on the alpha tracks, it is possible to obtain the velocity of an alpha particle at any point on the path." But how shall the velocity be found in the absence of forks and kinks? The answer is found in the application of a magnetic field. This changes the paths of the particles from straight lines to curved lines, and from the radius of curvature at a point can be calculated the ratio of the velocity of the particle at that point to the electric charge at that position upon it. To bend the path sufficiently a strong magnetic field is essential, and this requires a strong current. Since, however, the particle traverses with a velocity that is an appreciable fraction of the velocity of light the few centimetres in the length of its path, it is not necessary that this large current should flow longer than for a small part of a second. By using a special accumulator 8000 amperes were furnished to the coil of an electromagnet for .002 second. The brevity of the duration kept the current from fusing the coils. "In these experiments the field which was produced in a bobbin surrounding a circular Wilson chamber of 2.2 cm. in diameter, reached 75,000 gauss. . . . A special shutter which let the alpha particles into the expansion chamber only during 0.001 second is timed with the current in the coil." Photographs of the cloud tracks thus curved show that each track has a curvature of its own. The cause of this difference awaits an explanation. "About 8 mm. from the end of the range all behave in a similar way and have nearly the same average charge + 1.5*e*." This diversity in curvature may be discouraging to him who first noted it, but so much has already been learned from the kinks and bends of the tracks that one may well hope to gain fresh knowledge of the mechanism of collision from the interpretation of the tracks described in the magnetic field. G. F. S.

Hexanitrite Test for Lead. LAWRENCE T. FAIRHALL, of Harvard University (*Jour. Biol. Chem.*, 1923, **57**, 455–461), has studied the hexanitrite microchemical test for lead. This test depends on the crystallization of regular rectangular plates or cubes of the hexanitrite of potassium, copper and lead of the formula $K_2CuPb(NO_2)_6$ from an aqueous solution. The test will reveal the presence of as small an amount as 0.001 milligram of lead in 15 c.c. of a solution containing a considerable amount of other inorganic salts.

J. S. H.

THE MAIN PIERS OF THE BRIDGE OVER THE DELAWARE RIVER, BETWEEN PHILADELPHIA AND CAMDEN.*

I. DESIGN.

BY

CLEMENT E. CHASE, C.E.

Principal Assistant Engineer, Delaware River Bridge Joint Commission.

As THE first step in translating into actuality the century-old project for a bridge over the Delaware River between Philadelphia and Camden, the building of the two river piers has commanded special attention.

The completed piers are notable examples of massive granite masonry, conspicuous in a day when granite masonry has been largely displaced by hastier and cheaper all-concrete construction. The ashlar courses have a rise of from three feet five and one-half inches to two feet six inches, and individual stones weigh as much as nineteen tons. The lower half of the shaft exposed above water level is "rock-" or "quarry-face" ashlar; the upper half smooth finished—what the quarry man terms "four-cut." The proportioning of the mass was most carefully studied in relation to the design of the steel shaft of the tower that was to surmount it. As in all other parts of this structure, the attempt has been made to adopt that design which, within the limits of good engineering, would have the greatest architectural merit. The full measure of success with which that effort has met can only properly be judged when the bridge as a whole shall have been completed.

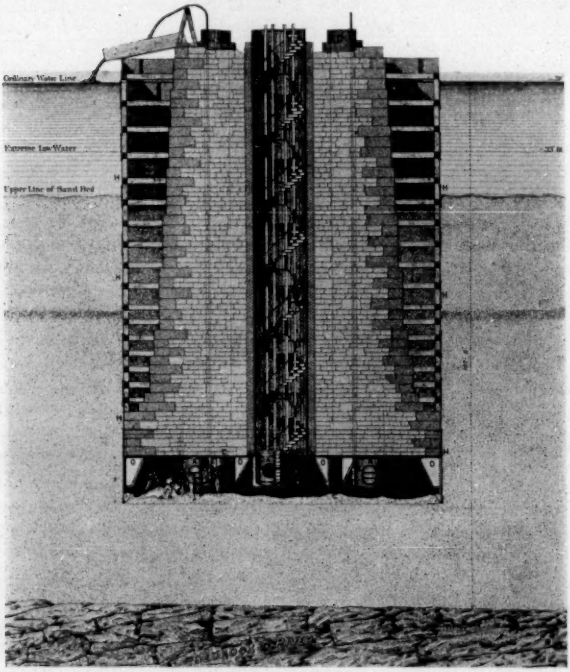
From the engineer's point of view, the principal interest in the two piers attaches to the means used in their construction—the design of the caissons and their handling during sinking. Passing attention, however, can be given to the conditions which governed the location and dimensions of the piers.

The Delaware, as a navigable stream, comes under the jurisdiction of the War Department. The terms of the permit signed by the Secretary of War required the bridge to span without piers

* Presented at the Stated Meeting of The Franklin Institute held Wednesday, February 21, 1923.

between the pierhead lines on the two sides of the river. At the selected location on the line from Franklin Square in Philadelphia to Pearl Street in Camden, this requirement fixed the span at

FIG. 1.



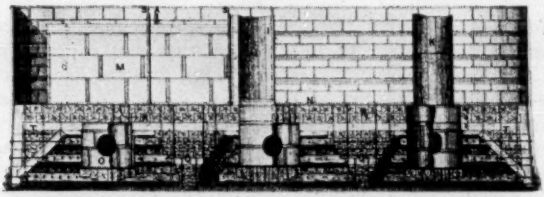
Caisson—east pier—Eads Bridge.

1750 feet, centre to centre of piers. Preliminary borings at this site had shown bed rock of good quality to be readily accessible by the ordinary methods of pneumatic caisson foundation. The length of the pier was determined by the necessary distance apart of the two main cables of the bridge and by considerations of procuring a proper width of masonry outside of the tower

bearings. The width of the pier had to be great enough to secure complete stability and prevent excessive bearing pressures at the edge from wind load and unbalanced cable pull. Each foot of additional width cost not only directly in masonry, but also indirectly in the increased span length involved.

During the design of the foundations and preliminary to the letting of the construction contracts, unusually thorough test borings were put down by churn and diamond drill methods over the entire area of each pier. These gave advance warning of irregularities in the level of the rock surface, knowledge as to

FIG. 2.



Caisson—east abutment—Eads Bridge.

the quality of the rock that would be encountered, and assurance that it was not underlaid with soft strata. Some of the holes penetrated thirty feet into the mica schist rock.

Bed rock on the Philadelphia side of the river was found to be from about 60 feet to 78 feet below mean high water and on the New Jersey side about 24 feet deeper. The complete information secured was of great assistance to bidders and to the successful contractors, in their handling of the work.

Alternate studies were made of foundations employing one large caisson or two smaller ones. In the latter case the difficulties and expense of securing a proper tying together of the pier shaft ruled out the scheme. With foundation by a single caisson for each pier decided upon, it was very apparent that the problem of adequate caisson design was a most important one. In Table I are given the sizes of a number of the largest pneumatic caissons that have been constructed for bridge foundations, showing those of the Delaware River Bridge to be fourth in size of those listed.

It may surprise some to note how much larger the Brooklyn Bridge caisson was than any built in the fifty years since.

TABLE I.

Date.	Bridge.	Dimensions.	Area in sq. ft.
1871	N. Y. pier, Brooklyn Bridge	102 × 172	17,544
1898	Alexander III Bridge, Paris	110 × 145	15,850
1901	Manhattan Bridge, New York	78 × 144	11,232
1922	Delaware River Bridge	70 × 143	10,010
1910	Quebec	55 × 180	9,900
1914	Metropolis	60½ × 110½	6,655
1869	East Abutment, Eads Bridge	72½ × 82 (hex)	6,000

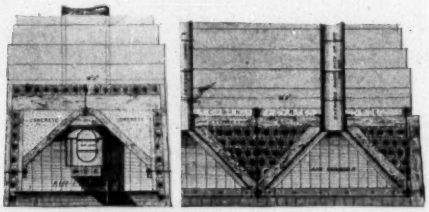
In those fifty years, however, great changes have occurred in pneumatic foundation practice. Much that was of the nature of a novel expedient in Brooklyn Bridge construction days has since become mere routine. Prof. Ira O. Baker tells of the interest aroused in Chicago at the time blasting was first proposed to be done under air in the Brooklyn caissons. The Chicago papers carried daily bulletins as to the success of the operation. To-day blasting under air is resorted to with as little ado as pick and shovel work. The ingenious but elaborate sand pump, developed by Eads, has been simplified until all is eliminated but the flexible hose, through which the mixture of sand and water, or air and water, is expelled from the bottom of the working chamber. Candles were at first the only source of illumination in the working chamber. These burned rapidly, with excessive smoke that blackened the lungs of the workmen. The open flames made the danger of fire a constant menace. Electric illumination has changed all this, and vastly improved working conditions. One is struck, however, with the fact that these improvements have been far more striking in technique and equipment than in the design of the caissons themselves.

Caisson design has much in common with that of ships; the forces are large and, to an even greater extent than in naval architecture, indeterminate. Construction has been governed largely by rule of thumb, and experience and precedent more relied upon than any analysis of the forces involved. Progress under these conditions is naturally a matter of slow development and improvement.

It would probably give a better perspective to a view of the development of caisson design to retrace briefly the history of pneumatic foundations.

The first suggestion of the process is to be found in the invention in 1717 by Doctor Halley, Secretary of the Royal Society of London, of a method for furnishing a continuous air supply to a diving bell. The idea, however, except for its use by Smeaton at Hexham Bridge, lay practically dormant for more than a hundred years until the great burst of engineering activity in England in the early nineteenth century served to turn men's minds to the

FIG. 3.

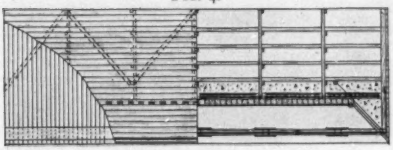


Caissons—east approach piers—Eads Bridge.

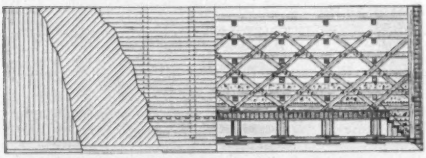
need for means of carrying on work under water, for the construction of tunnels, marine structures and bridge piers. In 1830 Thomas Cochrane, an adventurous Scotch nobleman and soldier of fortune, applied for a patent in which he fully set forth the essentials of caisson and air-lock as we now know them. His device was suggested by the difficulties which were then being encountered by the elder Brunel in the attempt to construct the first tunnel under the Thames.[1] In Woodward's history of the Eads Bridge, it is stated that Triger, a French engineer, made the first actual use of compressed air methods. This was in connection with the sinking of a mine shaft in the year 1841. Based on that experience, he later suggested the use of the same method for bridge foundations. Such a use was made of the new method at Rochester, England, in 1851, and in the United States in 1852, in the foundations of bridges over the Peedee and Santee Rivers. The foundations for these last were cast-iron cylinders,

[1] From memorandum by Daniel E. Moran.

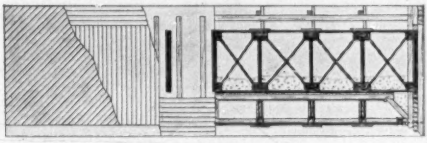
FIG. 4.



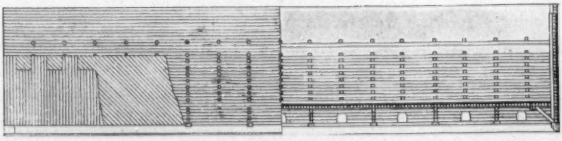
McKinley Bridge, St. Louis, Mo. Length 70′ 0″.



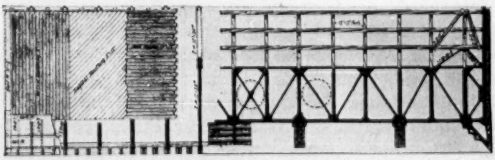
Municipal Bridge, St. Louis, Mo. Length 90′ 3″.



Metropolis Bridge. Length 110′ 6″.



Quebec Bridge. Length 180′ 0″.



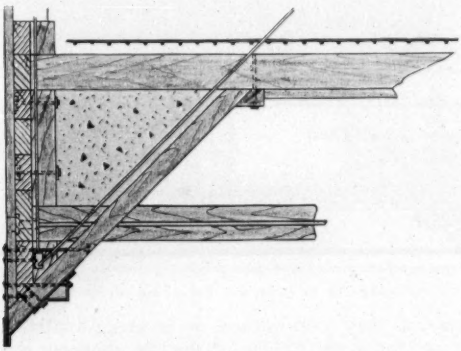
Delaware River Bridge. Length 143′ 0″.

Elevations and sections of caissons.

called "pneumatic piles." In 1854 Brunel used the scheme on a larger scale on his Saltash Bridge, and in 1859 it was used by St. Denis for the Rhine Bridge at Kehl. From that time on, the method grew in favor and was widely adopted in Europe.

In 1868, Captain Eads, in the first plans for his bridge over the Mississippi, proposed to found the main piers within open wells, sunk to bed rock by open dredging. On his trip to Europe, however, in 1869, he saw the river piers which were then being built at Vichy and talked with the resident engineer, M. Audernt, who had been building foundations by the pneumatic process for fourteen years, during which time he had put down forty bridge piers.

FIG. 5*a*.



McKinley Bridge, St. Louis, Mo. Caisson wall and cutting edge.

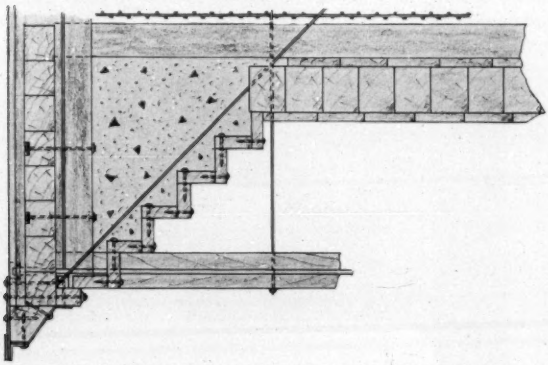
Eads also consulted with British engineers who had used the process and on his return to St. Louis in April, 1869, decided to use compressed air on the two river piers, though the depths to which these caissons must be sunk were greater than any hitherto attempted. No time was lost in carrying the plan to execution, for on October 17th of that year the caisson of the east pier was launched and between that date and April, 1871, the west pier and the east abutment caisson were also constructed by the same method.

These pioneers soon discovered for themselves many novel effects of work in compressed air. Woodward remarks that they found that one could not whistle and that candles burned very

rapidly, creating a great deal of soot. Some of the workmen shortly developed the ailment peculiar to work under compressed air and we can detect the origin of its common name, the "bends," in Woodward's narrative:

"A workman walking about with difficult step and a slight stoop was at first regarded as a fit object for jokes, and cases of paralysis and cramp soon became popularly known by the name of 'Grecian bend'"—then the mode of fashionable ladies.[2] The

FIG. 5*b*.



Municipal Bridge, St. Louis, Mo. Caisson wall and cutting edge.

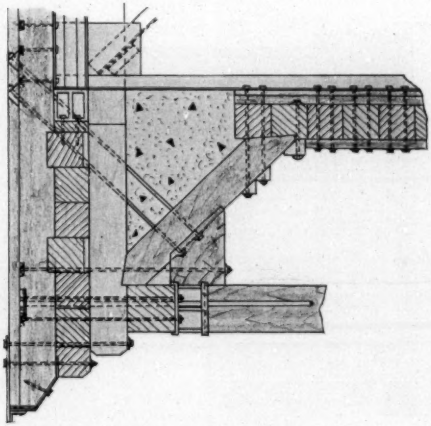
bends were, as they soon learned, no laughing matter, however, at that time, for in the sinking of the east abutment eleven men lost their lives from this cause. The "caisson disease" has been given much study since that time and the precautions by which its seriousness can be minimized have been well established. Special consideration was given to these in the drafting of the specifications for the Delaware River Bridge work.

At the same time that the work was going on in St. Louis, the foundations of the Brooklyn Bridge were being constructed in New York by the same process. The caisson for the Brooklyn pier was launched in March of 1870 and the New York caisson, which still holds the record of being the largest ever built, was launched in May of the following year.

[2] Woodward, p. 247.

The first caisson designed by Captain Eads followed the precedent of European practice in being largely constructed of metal. Wrought iron, at that time, cost from 6 to 7 cents a pound in this country. The same economic conditions which led later to the development of the typical American type of timber caisson, influenced the St. Louis Bridge work so that, by the time the third caisson was constructed, Eads had adopted timber roof

FIG. 5c.



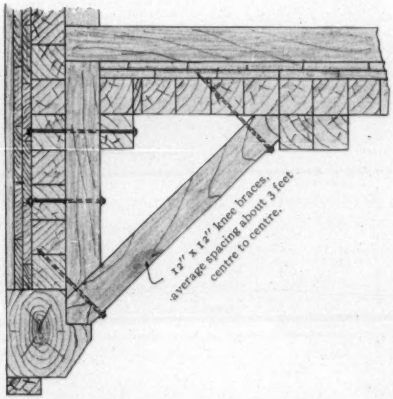
Metropolis Bridge. Caisson wall and cutting edge.

and side walls, though retaining a metal crib above the working chamber. Under American conditions it was quicker and cheaper to build caisson structures in timber than to secure the equivalent strength in metal. In their prodigal use of timber the Brooklyn Bridge caissons set another record which has held ever since. The caisson for the New York pier had twenty-two feet of solid 12 × 12 timbers over the working chamber for a caisson 102 × 172 feet in plan. Later American engineers tended to follow the lines of this precedent. William Patton, in the caissons for the B. and O. Railroad Bridge at Havre de Grace, used eight feet of solid timber above the working chamber for a caisson

only 31 × 79 feet in plan. The modifications in caisson design which have come since that time have been the result of changing economic conditions in this country and the growing development of other types of construction, such as reinforced concrete and structural steel.

In the development of the design for the Delaware River Bridge caissons, twelve distinct studies were made. The first of these was for all-timber construction, along conventional lines.

FIG. 5*d*.



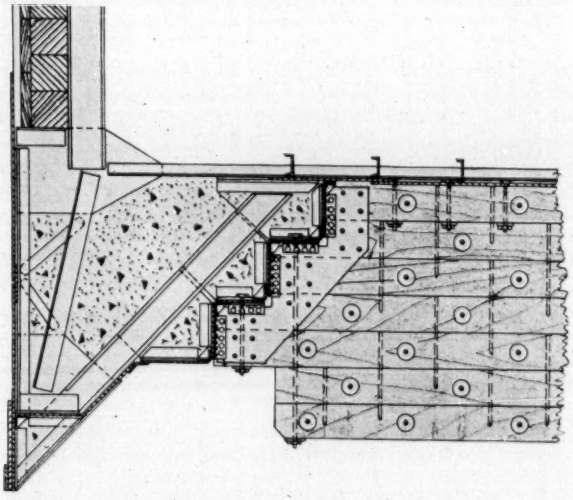
Quebec Bridge. Caisson wall and cutting edge.

The last, and adopted, design used steel for all parts except walls above the working chamber, the upper bracing and the cofferdams. So successful were these caissons in practice that the only regret of the designers has been that even the side walls and bracing were not also of steel. The design in its evolution followed a close parallel to the historical development of this type of structure.

To provide strength against longitudinal and transverse bending forces, the earlier caissons relied on their massive solid timber roofs and, later, on intersecting crib work built up above the roof. The caissons of the second Quebec Bridge were typical of this type of construction. The troubles which developed with the 180-foot

Quebec Bridge caisson during sinking would tend to show that in it, reliance on crib work for bracing had been carried to an extreme. This caisson, through a failure of its pumps, grounded prematurely on a bottom which had not yet been properly prepared, causing a sag at the centre of fifteen inches, later increasing to two and one-half feet. Eight feet of concrete, which had been

FIG. 5e.

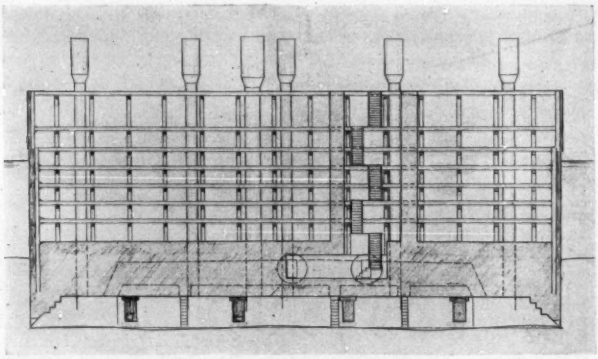


Delaware River Bridge. Caisson wall and cutting edge.

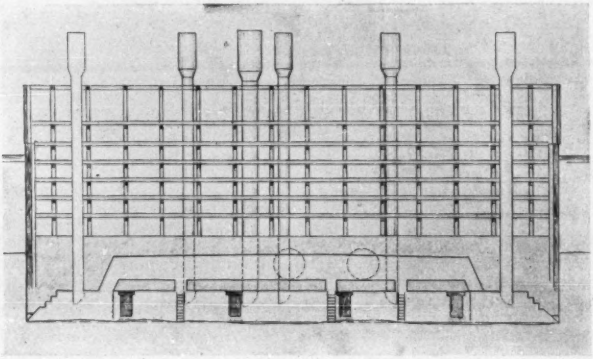
placed over the roof and in the interstices between the cribbing, had to be removed before the caisson could be refloated and taken back to dry-dock for repairs. It was found, on examination, that the caisson had landed on a boulder at one corner, setting up stresses which in all probability could not have been resisted by any caisson design developed up to that time.

Within the last fifteen or twenty years, the development of reinforced concrete has made its influence felt in caisson construction. All-concrete ones have been built, some of them quite successful in operation. Studies of this type were included

among those made for the Delaware River Bridge, but did not compare favorably with the other designs. A more limited use of reinforced concrete in combination with timber has been found



Caisson A—section through stairwell.



Caisson A—section through emergency chamber.

economical. In this type, quite largely developed by the Missouri Valley Bridge and Iron Company in the Middle West, reliance is placed in a reinforced concrete slab for the strength of working

chamber roof and side walls. In this way the thickness and amount of timber used has been materially reduced until it serves as hardly more than a substantial form, capable of standing launching stresses and resisting hydraulic pressure on the side walls above the concrete level. To secure greater rigidity of the timber construction at launching, diagonal braces were spiked and bolted to the longitudinal bracing of the St. Louis Municipal Bridge caissons. In the caissons for the Metropolis Bridge over the Ohio River, steel trusses were utilized above the roof of the working chamber. These proved very successful.

The first designs of the Delaware River Bridge made use of close timber cribbing of the Quebec type for interior bracing and stiffening. Later, combination trusses, with steel tension rods, cast-iron blocks and timber chords and posts were studied. On analysis of the design finally developed for this type of truss it was found that there was enough metal in each of them to make a good steel truss. With the favorable recommendation of the engineers who had sunk the Metropolis caissons, steel trusses were adopted as soon as satisfactory details had been developed. Main reliance for stiffening the roof was placed in the transverse trusses, the longitudinal system being considered merely as distributing girders. The main longitudinal strength of the caisson lay in the side walls, with their double layer of sheathing.

With steel trusses decided upon, the use of a steel roof for the working chamber followed naturally, as it cost about one dollar less per square foot of roof and entirely eliminated the fire danger, which is always present in the timber roof.

With steel adopted for working chamber roof and the trusses above, the next step was the development of a steel working chamber wall or "toe," filled and stiffened with concrete after launching. Above the working chamber the timber walls of the earlier designs were retained.

Retracing the historical development of this element of the caisson, we find that Eads in his first St. Louis Bridge pier used a metal cutting edge, an iron shell braced by riveted iron brackets. In the succeeding piers of that bridge V-shaped walls were used, either of solid timber or of timber, concrete filled. In the later extensive use of the pneumatic caisson by American engineers both the V-shaped walls and parallel side walls of timber were utilized. G. S. Morison used 17 × 17 inch timbers for the

inside sloping wall of his Bellfontaine Bridge caissons in 1892. The parallel-sided timber walls, however, were even more commonly used despite the fact that partial failures of this type of wall have quite frequently occurred during sinking. In the light timber and concrete caissons previously referred to, the Missouri Valley Bridge and Iron Company adopted the V-shaped toe filled with concrete and reinforced with steel rods. Their St. Louis Municipal Bridge caissons had a stepped inner wall because of the engineer's objection to a possible cleavage plane which might be produced in the finished pier by an inclined surface. All these types of caisson wall have depended very largely upon interior bracing across the working chamber for their strength, especially so in the case of the parallel-sided timber walls. Recent examples were the Metropolis and Quebec caissons, and in both cases there was evidence of overstress in bracing or wall timbers, or both, during sinking.

The great advance in the design of the walls of the Delaware River Bridge caissons was in making them self-supporting, thus freeing the working chamber of the obstruction of cross-ties and braces. The four bulkheads which divided the working chamber into five compartments were provided only for support of the caisson during sinking and did not brace the side walls. The change to steel design permitted the use of steps in the inner face of the caisson wall and made the actual cutting edge itself more accessible.

Even without bracing in the interior of the working chamber, the toes of these caissons were much stronger than those of most

TABLE II.

Comparison of Strength of Caisson Working Chamber Walls.

Caisson.	Outward thrust per foot in lbs.	Inward thrust per foot in lbs.
Quebec Bridge (1910)	2,000	26,000
Manhattan Bridge	5,000	36,000
Metropolis Bridge	7,000	87,000
Delaware River Bridge	55,000	70,000

of their predecessors. Table II gives the thrust in pounds at the cutting edge, which each of several notable caissons would have resisted at safe working stresses, per foot of working cham-

ber wall, or toe. It will be noted that the Delaware River Bridge design is the only one which has a toe almost as strong against outward as inward thrust.

Bulkheads similar to those used in the Delaware River Bridge caissons had been employed in the Quebec Bridge caissons with satisfactory results.[3] They make it possible to carry the entire weight of the caisson and the completed portion of the pier on bearing under these bulkheads instead of on the cutting edge as would otherwise be necessary. This is a great advantage in controlling the sinking and in carrying the caisson through heavy boulders or into rock, without damage to the walls of the working chamber.

Another unusual feature of these caissons, required by the specifications, was the emergency chamber, located above the roof of the working chamber in the mass concrete. This was planned to serve as a place of refuge for the entire shift, in case of blow-out or other accident in the working chamber, until the men could be locked out. It had access to each of the five compartments of the working chamber by separate manholes through the roof, each provided with a ladder. It had its independent source of air supply but would have served as an air reservoir, on the principle of the diving bell, even in case of failure of the air supply. In actual use, fortunately, no emergency developed. The chamber nevertheless served a very useful purpose as a communicating gallery, by which the men reached the compartment in which they were to work without the necessity of passing through successive bulkheads. The emergency chamber clause was one of several in the specifications, inserted to safeguard the men working under air, the details of executing which were left to the contractor, subject to the approval of the engineer. Another was the provision at the refuge chamber level of emergency locks, capable of holding an entire shift at one time. A stairway in a water-tight open shaft led from these locks to the surface.

What was planned to be the regular service man lock was above water, at the top of a four-foot shaft, which was equipped with an elevator hoist bucket. Actually the large tunnel

[3] The pump pit caissons for the waterworks of the City of Cincinnati, built in 1898–99, used a number of cross-bulkheads designed with cutting edges, but changed to act as bearing walls only. . . . the first definite use of cross-walls as carrying walls pure and simple.—*Memorandum by Daniel E. Moran.*

locks, which were installed just above the roof of the working chamber as the emergency locks, were used and this elevator hoist neglected.

The contract drawings for the caisson showed typical cofferdam sections, designed so that they might be detached from the caisson proper on completion. On the western rivers, the masonry of the pier shafts is quite commonly started before the caisson is sunk to its final elevation, and laid as fast as sinking progresses, so as always to keep the top of the masonry above water. With this practice no cofferdam is needed, except possibly until the caisson is firmly landed. On the Delaware River Bridge work the contractors preferred to complete the sinking before starting the masonry, thus insuring that the pier shafts would be exactly in correct position without any offsetting of the masonry courses and also that only the minimum amount of granite masonry would be required. They accordingly provided sufficient cofferdam to reach from the top of the caisson proper to above high water level. Only the top section, above the level of the bottom of the granite-faced portion of the pier, was made removable. The others were narrowed up, so as to act also as forms for the concrete portion of the pier shaft, and were left in place. The Camden caisson had 33 feet of cofferdam, left in place, and a 15-foot removable section.

The care given to the design of the caisson and preparation of the specifications probably deserves to share credit with the skill and experience of the construction organization for the smooth and rapid manner in which the actual field work went forward. The behavior of the caissons under the test of launching and sinking was a source of satisfaction to all those of the engineering staff of the Joint Commission who had had a part in their design.

II. CONSTRUCTION.

BY

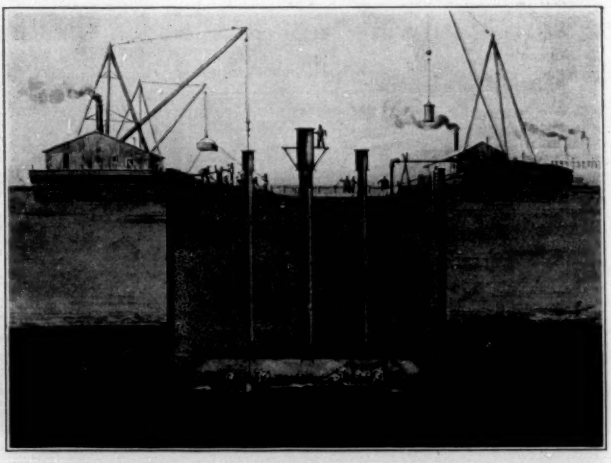
MONTGOMERY B. CASE, B.Sc., M.A.Soc.C.E.

Senior Resident Engineer, Delaware River Bridge Joint Commission.

AT MOST locations where deep pneumatic bridge piers are to be built, one of the first problems is the selection of the method of supporting the caisson during construction and of launching it after it is ready to be floated.

This problem is frequently complicated by a considerable range in the stage of the water. At many locations on the Ohio, Mississippi and Columbia Rivers this range amounts to as much as 40 to 60 feet. Under such conditions the length required for inclined launch-ways, where the banks are flat, often makes their cost prohibitive, unless there are a number of caissons to be launched. Caissons of moderate size have been floated by means

FIG. 1.



Sketch of typical pneumatic caisson foundation.

of lowering on large screws suspended from trusses supported on barges alongside the caisson. Larger caissons have been floated from pontoons built on the style of a primitive floating dry-dock. For piers near the bank or in shallow water, the caisson is sometimes supported during construction by filling the site to an elevation above the water surface and later sinking the caisson through this supporting fill.

For the piers of the Delaware River Bridge, it was fortunate to have several large shipyards with launch-ways capable of supporting a battleship, in close proximity. The plant and experi-

enced personnel were also a large factor in greatly reducing the cost and the time necessary to construct the caissons and launch them ready for sinking.

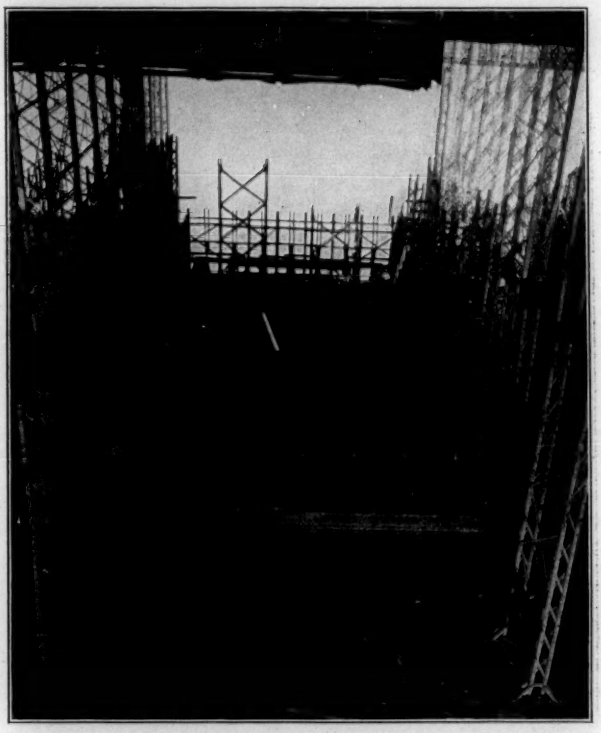
FIG. 2.

Side wall and roof plates in place on the building ways.

The adopted design, described by Mr. Chase in the previous paper, with steel cutting edges and steel-plated sides and with the roof of the working chamber supported by steel roof trusses, was in effect merely an inverted steel barge with a timber struc-

ture or crib rising above the chamber (Fig. 2). This construction lent itself admirably to the plant, tools and experience of a shipyard. The contractors for the two main piers of the Delaware

FIG. 3.

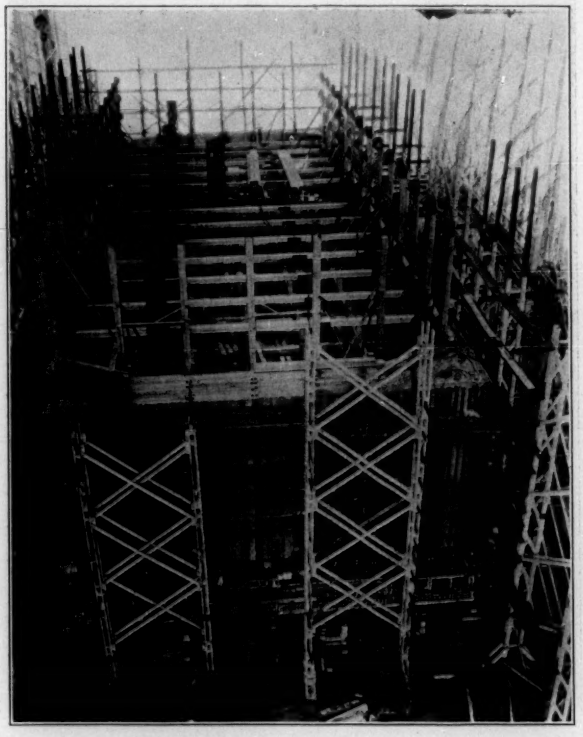


Caisson B showing 6½ courses wall timbers in place.

River Bridge, Holbrook, Cabot and Rollins Corporation, of Boston, and the Keystone State Construction Company, of Philadelphia, acting jointly, selected the New York Shipbuilding Corporation to construct the caissons.

The fact that these caissons could be constructed to their finished height (Fig. 5), ready for sinking to their final depth, before they were launched, was in striking contrast to most situa-

FIG. 4.

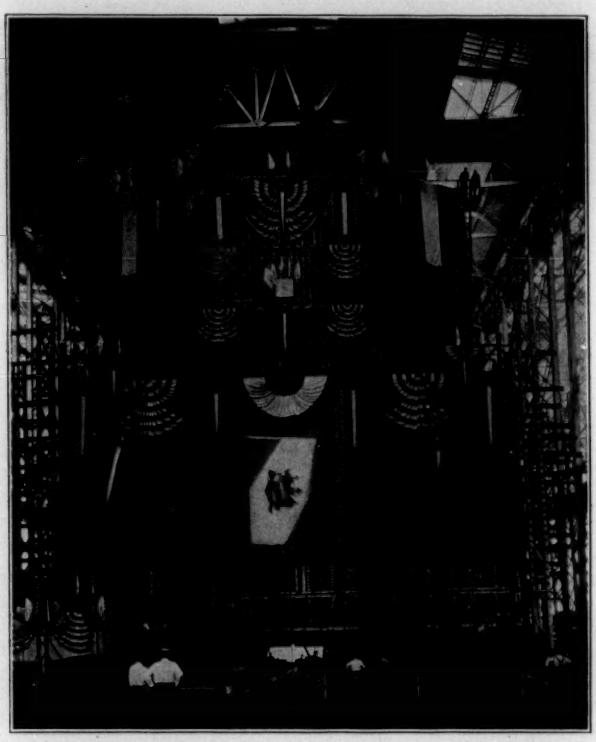


Caisson B erection progress.

tions, where the crib or structure above the working chamber is built up as the sinking proceeds. The rate of sinking is often limited by the rate at which the crib can be built up to keep it

above the water surface. The construction of the crib during sinking operations also adds materially to the complication of carrying on so many operations in a limited space.

FIG. 5.



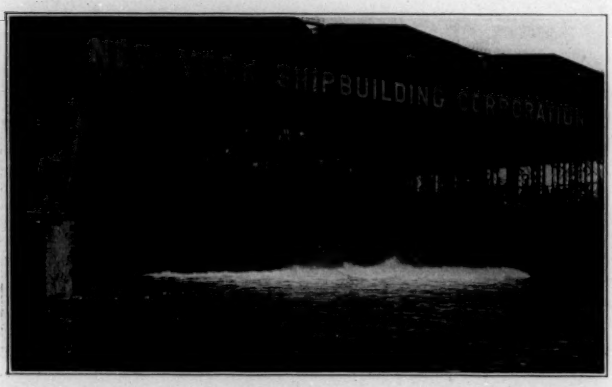
Caisson B ready for launching.

While the caissons were being constructed at the shipyard the sites of the piers were dredged to a depth of forty feet below mean high water. This excavation, even with the larger quanti-

ties involved in the side slopes, could be made more cheaply by dredging than by excavating the smaller volume within the area covered by the caisson under air pressure. This procedure was also an advantage, but such a method could not be used on many rivers with a swifter current and a shifting sand bottom where the dredged excavation would be filled by the current before the caisson could be settled on the bottom.

The plant provided for sinking the caissons was almost identical on the two sides of the river, but arranged somewhat differently

FIG. 6.



Launching of caisson A.

to meet the local conditions. On the Philadelphia side the plant was all located on the river end of Pier No. 11, North Wharves (Fig. 13). Six compressors, with a total rated capacity of 5000 cubic feet of free air per minute, were provided. One of these could be operated as a high-pressure machine to furnish pneumatic power for the rock drills in the caisson. Six one-hundred horsepower boilers were provided, which also furnished steam for two one-yard concrete mixers, hoisting engines, pumps and other auxiliary machines. Air was carried from the receivers to the caisson by two four-inch and two six-inch pipe lines, laid along two independent routes. Every pipe line entering the caisson working chamber was protected by a gate valve where the

line left the dock, and in addition to this the air supply lines were provided with a check valve at the top of the caisson and with a clapper valve at the roof inside of the working chamber.

While the five compartments formed by the four bulkheads were at all times interconnected by the two open passages through the bulkheads and by the clear working space along the cutting edge at the ends of the bulkheads, the precaution was taken of having one of the air supply lines enter each of the compartments

FIG. 7.

Towing caisson B into position.

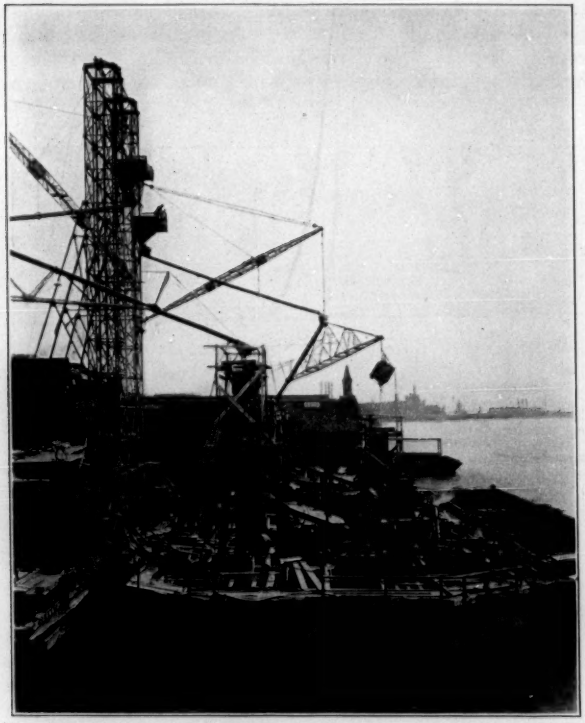
except the centre one. An air supply was provided just above the roof of this compartment in the refuge passage at the inside door of the man locks.

These conditions were the same for the caissons on both sides of the river. The principal difference in the arrangement of the plant on the two sides of the river consisted in the location of the compressors in Camden back at the street line, some fourteen hundred feet from the caisson. The towers for hoisting concrete were at the end of the caisson on an adjoining pier (Fig. 11), requiring somewhat longer distributing chutes than in Philadelphia, where the concrete towers were on the end of Pier No. 11 near the centre line of the bridge.

When the caissons were launched they weighed about 1800

tons and drew twelve and one-half feet of water. The site having been previously dredged to a depth of forty feet below mean

FIG. 8.

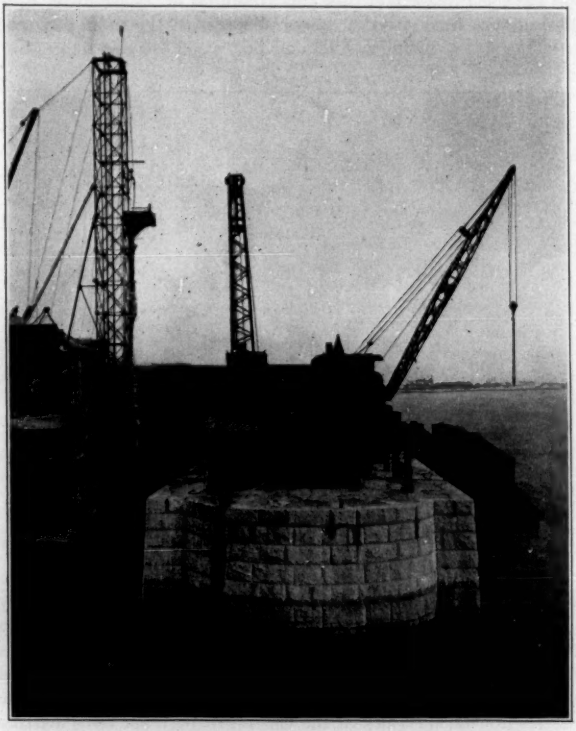


Caisson A in permanent position, view from Pier 10. The lock on the right is handling muck, on the left the hoisting sheave has been removed and the concrete lock applied preparatory to sealing.

high water, it was possible to sink the caisson twenty-seven and one-half feet by the addition of concrete load before the cutting edge came in contact with the river bed.

This loading permitted a depth of twelve feet of concrete in the crib over the roof of the working chamber and brought it to within three feet of the top chord of the steel stiffening trusses.

FIG. 9.



Pier A, looking north, showing method of handling granite.

This reinforced concrete slab, in addition to the trusses, thus made it possible to obtain considerable rigidity against warping while the caisson was still floating. Before air pressure was applied, which increased the flotation by the displacement of the

water in the working chamber, it was possible to bring the concrete over the top chord of the trusses, thus insuring a very rigid structure to resist the forces set up by the bearing on the bulkheads and cutting edge.

On the Philadelphia side this condition of approximate equilibrium was maintained at most all stages of the sinking so that

FIG. 10.

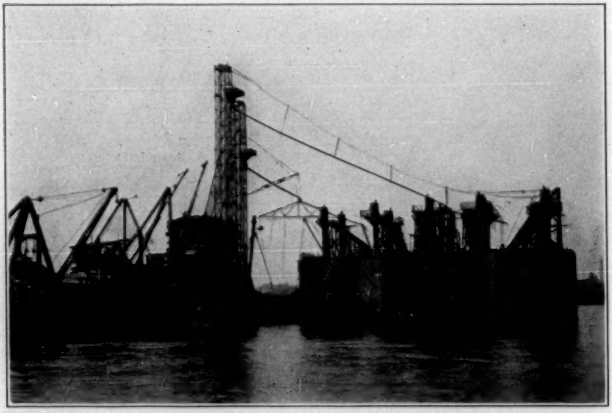
Pier A, southern end, showing granite construction.

the caisson structure was at no time called upon to carry any great load at the cutting edge. In fact, on three occasions, when the daily computations of load and reactions were made, it was found that there was a positive uplift, in one case of one hundred and fifty-six tons at high tide. This uplift was either resisted by the friction on the sides of the caisson or may not have actually existed, since the gross weight of the caisson was at this time in excess of 17,000 tons and an error of less than 1 per cent. in the assumed unit weights or the recorded quantities would account for the difference.

With a tide of five or six feet, the cutting edge necessarily

came to bearing several times before sufficient concrete could be placed to hold the caisson down at high tide. This made the mooring in accurate location more difficult, but when the Philadelphia caisson was firmly on bottom the position of the upstream end was two inches west of true position, the downstream end was one foot east, and the centre was four inches upstream from the bridge axis. During sinking this location was changed to a

FIG. 11.



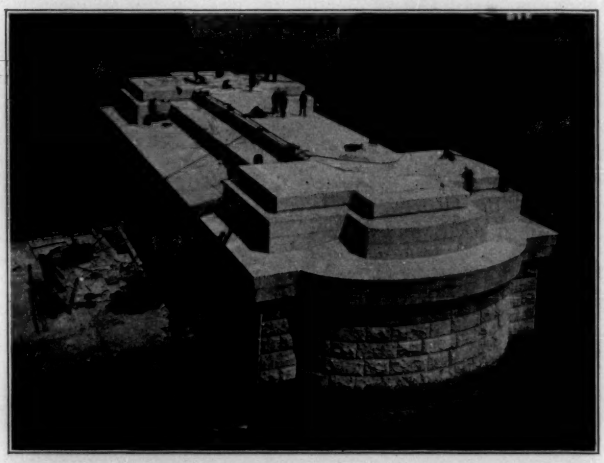
Caisson B from Stockham wharf, showing Matison muck locks in place. The muddy streaks are from the blowpipes.

skew of eight inches at the time of sealing, which was well within reasonable tolerance for a caisson 70′ × 143′, and offered no difficulties in placing the granite masonry on correct location within the cofferdam. The cutting edge was eight inches out of level across the diagonal and at an average elevation –60.65. The datum plane used is that of the City of Philadelphia, which is 2.43 feet above mean high water in the Delaware River, as determined by the United States Engineer Office.

The Camden caisson was grounded with the upstream end on true position, the downstream end was two inches east of position and the caisson was less than one inch upstream from the centre

line. The cutting edge was less than eleven inches out of level across the diagonal. When sunk to final position the location at the base of granite was correct at the upstream end, three and one-half inches east at the downstream end and one and one-half inches upstream from the centre line. The cutting edge was four

FIG. 12.



Pier A, looking northeast, Philadelphia side.

inches out of level across the diagonal and at average elevation –84.83.

No objectionable warping of the plane of the cutting edge or distortion of the side walls of the working chamber was found at any time during the sinking of the Philadelphia caisson. The Camden caisson was, therefore, handled with considerably more load which assisted in speeding up the excavating and sinking, in that the trenching along the cutting edge was less tedious. The general practice followed was to carry the net weight or unbalanced load on pillars of undisturbed material under the bulkheads. After mucking had progressed to a point where the caisson ceased to follow down, the pillars were robbed and reduced in area so that they would crush and permit the caisson to settle.

Most of the excavated material was removed from the working chamber by hoisting in buckets through the muck shafts (Fig. 1). Some sand and gravel were blown out through the six-inch pipes. This operation is accomplished by feeding a mixture of water, sand and air into a flexible but non-collapsible hose which is attached to the pipe at the roof line. If the operator allows the lower end to remain constantly submerged, a solid column of

FIG. 13.

Aerial view both sides of river.

water and sand is fed into the pipe which, being no lighter than the hydrostatic head, balanced by the caisson air pressure, the water column soon comes to rest and the solid material, settling back, plugs the pipe. On the other hand, too much air fed into the pipe is wasteful of power, reduces the rate of discharging excavated material, and in extreme cases would result in lowering the caisson pressure sufficiently to cause a premature settlement.

In the hands of an experienced operator the blowpipe is by far the most rapid and economical method of removing sand or gravel. Stiff or hard clay and broken rock must be locked out through hoisting shafts.

Each of the ten three-foot diameter muck shafts was equipped with a Matison type lock which proved very efficient (Fig. 8 and Fig. 11). These locks have the upper door opening in the cylindrical shell of the lock. The door is hung from a track riveted around the circumference of the top of the lock above the door opening. The door is curved to the same radius as the shell of the lock and is rolled open or shut like a barn door by means of a countersunk handle in the outside face of the door. The lower door is hinged and is swung up into a horizontal plane by means of a lever on the hinge shaft which passes through a stuffing box. Both doors seal on three-eighth inch rubber packing. Thicker packing is not desirable because it would expose a greater edge area to the pressure, and experience has shown that it more frequently blows out from under the packing ring or the contact surfaces between the door and the seat. The hoisting cable passes up through a packing gland centred over the hoisting shaft in the top of the lock. When the fourteen cubic-foot bucket of clay is hoisted up from the river bed, at the bottom of the working chamber, into the lock, the bottom door is swung up under the bucket, the air pressure is released from the lock into the atmosphere and then the pressure being relieved on the upper door, it can be rolled open and by slacking on the hoisting line the bucket of muck is dumped out through the door into the chute which carries it overboard into a barge for disposal.

The bed rock surface was very sharply defined under the Philadelphia pier and is a mica schist with strata upset at an angle of 60 degrees with the horizontal. The surface was generally level along the east side of the caisson. Along the west side, the rock sloped down from one foot below the cutting edge at the southwest corner to eleven feet at the northwest corner. Careful soundings showed that the rock surface was not below this depth at any point. To avoid the larger volume of rock excavation it was decided to underpin the west cutting edge with a concrete wall down to rock without sinking the caisson further. This underpinning was done by trenching in ten-foot alternate sections longitudinally and in about three-foot depths vertically, so that at no time was more than a three-foot height exposed to air leakage or possibility of a blow-out. The additional precaution was taken of packing the exterior face of the trench with stiff plastic clay as rapidly as the sand was exposed. The operation was entirely

successful and the balance of the rock surface could then be cleared off, ready for sealing the working chamber with concrete.

Very little of the surface of the rock was disintegrated enough to require removal. The maximum depth of rock excavation on some of the high points was about eight feet. Drilling and blasting was carried on without difficulty. At the time of blasting the electric light cords were taken up into the refuge passage by the crew, who remained in the passage under the air pressure without locking out.

The sealing of the working chamber was accomplished by locking concrete in through the muck shafts. This required 3200 cubic yards of concrete. It was not sent down in buckets, but allowed to fall from the bottom door of the concrete locks.

These concrete locks were installed by removing the top ring on the muck locks, which ring carried the hoisting sheave and packing gland (Fig. 8). The concrete lock was then bolted in place through the same holes that had been used to bolt the top ring. The top door of the concrete lock was hinged and swung up into a horizontal plane by means of a hand line. The bottom door was also hinged and swung into a horizontal plane across the eighteen-inch bottom opening of the concrete lock. In operation this bottom door was handled by a man who entered through the side door of the muck lock and worked his shift under pressure. His duty was to clean the packing gasket after each batch of concrete and, after lifting the door, to signal for the lock to be equalized out for the next batch.

After the concrete had been brought up to within four feet of the roof, the precaution was taken of concreting through both shafts in the same compartment simultaneously. All pipes entering through the roof were cut off flush so as to avoid air pockets along the ceiling and as the concrete surface approached the ceiling these pipes were occasionally blown to relieve any air pockets and permit the concrete to flow towards the pipes located in the corners of the compartment. Grouting operations, after the sealing was completed and the caisson pressure removed, showed that the sealing was entirely successful.

The Philadelphia pier was sealed with the cutting edge at elevation –60.65 when the immersion at high tide was fifty-eight feet and the air pressure was twenty-eight pounds per square inch. The gross weight of the caisson was 20,000 tons.

The sinking operations on the Camden pier differed principally in the nature of the material passed through and the greater depth. Between elevations −52.0 and −63.0 an eleven-foot stratum of hard blue clay was passed through. Underlying this the material changed gradually to sand and gravel, then to sand, mica and clay, and then to a mica schist, which was disintegrated. This material increased in hardness gradually until rock was encountered which could not be removed without blasting, and which was satisfactory for the foundation.

The Camden pier was sealed with the cutting edge at elevation −84.83 when the immersion at high tide was eighty-two feet and the air pressure was thirty-four pounds per square inch. The gross weight of the caisson was 30,500 tons.

A careful medical examination was made of all applicants for employment under compressed air. The men of the engineering staff who were assigned as inspectors under compressed air were also given the same rigid examination. A doctor was in constant attendance at the pier at all times while the caissons were under pressure. Bristol recording gages on the man locks greatly assisted in enforcing the rules laid down as to the rate of decompression in the locks.

The time required for locking out men was:

5 minutes from 15 pounds pressure,
10 minutes from 20 pounds,
18 minutes from 30 pounds,
and 25 minutes from 35 pounds.

The lock-tenders usually endeavored to release the last few pounds very gradually. An exception was made in the case of lock-tenders or workmen coming out to take tools or supplies into the lock where they returned immediately into the pressure. In this case they frequently came out in but a few minutes, but returned at once to the pressure.

The working period at pressures less than twenty pounds was eight hours in two shifts of four hours each with an hour intermission between shifts. From twenty to thirty pounds, six hours in two shifts with an intermission of three hours. From thirty to thirty-five pounds, two shifts of two hours each, with a two-hour rest period between shifts.

These regulations, in some cases, were slightly more con-

servative than the requirements of the industrial law of Pennsylvania or New York.

Great credit is due to the contractors for the success with which the work was carried out without a fatality from any cause and with a remarkably small number of minor injuries.

On the Philadelphia side there were 10,500 decompressions with only one case of bends for each 617 decompressions. On the Camden side there were 15,500 decompressions with one case for each 320 decompressions. The symptoms usually appeared in less than three hours after locking out and were relieved by recompression in the hospital lock, followed by a very slow decompression. The higher rate on the Camden side was probably due largely to a higher proportion of less experienced men who reported the symptoms when they appeared. The older men frequently conceal any light attacks to avoid possible loss of time if ordered off the shift. The higher air pressure carried would also be a contributary cause and is reflected in the record showing the largest number of cases at twenty-three pounds on the Philadelphia side and at thirty pounds on the Camden side.

A further probable contributing cause was the smaller quantity of air per man used on the Camden side. The ten-foot clay stratum passed through on that caisson served to act as a tight seal reducing the amount of air passing under the cutting edge. On many occasions when the locks were not in active operation the precaution was taken of opening vent pipes to insure a larger quantity of air for ventilation. While the plant was not equipped with meters, a careful estimate from the compressor operating records indicate that about twenty-two cubic feet per man per minute was supplied on the Philadelphia side, while on the Camden side the maximum was about sixteen cubic feet, the minimum twelve cubic feet, and under average conditions the air supply was fifteen cubic feet per man per minute. These quantities are quite approximate.

Temperature Coefficient of the Refractive Index of American Turpentine. GARTHA THOMPSON (*Analyst*, 1922, **47**, 469) has determined the temperature coefficient of the index of refraction of authentic samples of American turpentine, using sodium light and the Pulfrich refractometer. The coefficient ranged between 0.000468 and 0.000470. J. S. H.

The Recording Ultra-micrometer. J. J. DOWLING. (*Phil. Mag.*, July, 1923.)—"It will, of course, be understood that an apparatus which records small capacity variations will be immediately suitable for measuring minute movements, inasmuch as the capacity of a condenser varies with the separation of the plates." A condenser is joined to an oscillating valve circuit. If it is composed of two circular discs 5 cm. in diameter, separated by a distance of .025 cm., then a change in the distance between them of 1/10,000 cm. should produce a change in the anode current of 8 micro-amperes. A galvanometer joined in a special manner should show a deflection of 800 divisions for this current.

The instrument has found application in several cases. The two condenser plates, circular discs, 10 cm. in diameter, were clamped to a steel rod, 12 mm. in diameter, passing through their axis. When weights were placed upon the rod, it was compressed and the distance from the clamp supporting the upper plate to that supporting the lower was made less. This distance was initially 5 cm. The addition of 2 kg. produced a deflection of 121 divisions on the galvanometer. From the elastic constants of the steel it is found that one such division corresponds to one ten-millionth of a centimetre. The promptness with which the apparatus responds to the application of forces tending to change the distance from plate to plate was tested by using it to record the growth of the root-tip of a plant. The lower plate was rigidly supported, while the upper one was carried by a spring. The root-tip growing downward pressed upon it and moved it nearer to the lower plate. "The growth pulses noticed by Bose are shown very convincingly."

Again, one condenser plate was held in a horizontal plane by a spring stretched by a weight of 1 kg. hung from it by a silk cord passing through a hole in the lower plate just beneath. When 50 kg. of lead were brought near to the suspended kilogram the gravitational attraction pulled the movable plate down far enough to make the galvanometer deflect through 300 divisions, though the displacement was of the order of one eight-millionth of a centimetre.

The author is engaged in studying rapidly changing stresses in machinery with the aid of the instrument he has devised.

G. F. S.

Complex Cyanides. GEORGE JOSEPH BURROWS, of the University of Sydney (*Jour. Chem. Soc.*, London, 1923, **123**, 2026–2029), has studied the cryoscopy and conductivity of aqueous solutions of sodium ferrocyanide, potassium ferrocyanide, potassium ferricyanide, potassium cobalticyanide, and potassium chromicyanide. The results indicate that each of these salts yields cations of the alkali metal and a complex anion containing six cyanogen groups and an atom of either iron, cobalt, or chromium. This anion may undergo further electrolytic dissociation into simple cyanide anions and a metallic cation.

J. S. H.

IONIZATION AND RESONANCE PHENOMENA.*

BY

CHARLES B. BAZZONI, Ph.D.

Professor of Experimental Physics, University of Pennsylvania, Philadelphia, Pennsylvania.

THE quantum theory of radiant energy, which was originated by Planck in 1900 in an attempt to explain the distribution of energy in the spectrum of a completely absorbing body, has since that time been extended to cover an important fraction of the entire field of physics. This theory which postulates that energy in the form of radiation is not continuous in structure but is made up of discrete bundles or quanta each of magnitude $h\nu$, where h † is a constant and ν is the frequency of the radiation, has been applied in two main fields. The first of these fields is the field of black-body phenomena, atomic heats and the kinetic gas theory. The second field is that covering the interaction of radiation and matter—both the stimulation of radiation from matter through the impact of electrons on it and the stimulation of the electrons of matter by the absorption of radiation in it. Research in the second field has been especially successful in throwing light on the structure and on the dynamics of the atom. This paper deals with certain subjects lying in that second field being concerned mainly with the interpretation of the theories of spectrum production and absorption.

The first successful application of the quantum idea in the study of spectra was involved in Bohr's theory of atomic structure and the mechanism of radiation which was published in 1913.[1] In order to introduce our subject properly it will be necessary to summarize briefly the main points of that theory. It will be recalled that Bohr developed Rutherford's idea that atoms consist of aggregations of positive and negative electricity—an exceedingly minute nucleus with a net positive charge equal to its so-called atomic number being surrounded by a sufficient number of negative electrons exactly to neutralize it in the normal state. These electrons are supposed to move about the nucleus in paths

* Presented at a meeting of the Section of Physics and Chemistry of The Franklin Institute, held Thursday, March 8, 1923.

† h equals 6.554×10^{-27} ergs seconds.

consistent with the laws of classical mechanics with this vital and as yet unexplained exception that an electron moving in a fixed configuration loses no energy by radiation. Further, it is assumed that only such particular states of motion are possible in which the angular momentum of the electron about the nucleus is some integral multiple of $h/2\pi$. As a consequence of these assumptions the energy of any particular system of motion, that is a system with fixed radii of electronic orbits and an angular momentum equal to $nh/2\pi$, is invariable, and energy can be given out or absorbed by an atom only through a swelling up or shrinking down of the system from one stationary state to another. The fundamental idea of the Bohr emission and absorption theory may consequently be stated as follows: The energy radiated or absorbed by an atom in passing from one stationary state to another equals the difference of the energies in the two states, $W_2 - W_1$, and is in all cases equivalent to one quantum, $h\nu$, of monochromatic radiation of frequency ν.

For an atom having one electron only, the energy, W, of a particular state is easily found to be represented by $W = -2\pi^2 m_0 e^2 E^2/h^2 \times 1/n^2$ where m is the mass of the electron and e its charge. E represents the positive charge on the nucleus and n is the integer showing which multiple of $h/2\pi$ represents the angular momentum of the electron in the particular state considered. This n clearly specifies the successive possible orbits which the electron can occupy and is consequently frequently called the "orbit number." From this energy expression we may write, since $h\nu = W_2 - W_1$, $h\nu = -2\pi^2 m_0 e^2 E^2/h^2 (1/n_2^2 - 1/n_1^2)$ to represent the energy radiated when the atom passes from one stationary state to another. This last formula may be written $\nu = NZ^2 (1/n_2^2 - 1/n_1^2)$ in which N is the Rydberg constant * and Z is the atomic number $(E = Ze)$. The series of possible frequencies to be obtained from a simple atom of this sort is given by taking different combinations of the n's representing the electron jumping between the corresponding orbits. These frequency values will also represent the radiations which can be absorbed by the atom. This formula ought consequently to express the successive lines in the bright line spectrum and also in the absorption spectrum of an atom which has a single electron. As a matter of fact the formula, being identical with the famous Balmer formula, does

* Rydberg's constant is 109,737.7 for a heavy nucleus.

give the lines of the hydrogen spectrum with extraordinary accuracy. It will be observed that the frequency of each line in the spectrum is here given by the difference of a pair of quantities which are determined by the energies of particular orbital motions and that with, for example, ten such quantities we could predict, speaking generally, some forty-five lines.

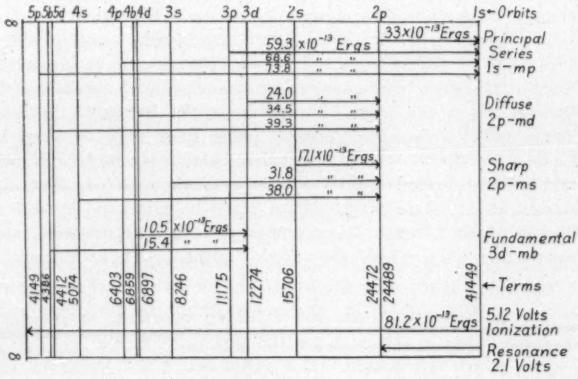
Let us next consider the formulas which have been developed from Balmer's formula by the spectroscopists for exhibiting the relations of the lines in spectra. When a fairly complex spectrum such as that of an alkali metal is examined, we observe certain series of more or less regularly spaced lines which have common visual characteristics so that we can distinguish series of sharp lines, series of diffuse lines and so on. The four most important series of this sort in the spectra of the alkali and alkaline-earth elements are, in the order of importance, the Principal, Diffuse, Sharp, and Fundamental series. These lines may be singlets, doublets or triplets—the total number being very large. It was found, years before Bohr's theory was thought of, that the frequencies of all these series lines could be expressed by differences between a much less number of other frequencies, not representing lines, which are called "terms." These terms can be calculated from expressions of the form $\nu = \frac{N}{(m+a)^2}$ where N is a universal constant, the Rydberg constant, m is given successive integral values to get the successive terms and a is a fraction which is constant for a given series and different for different series. The value of a is calculated from the observed lines. In the four important series just mentioned a is specified by P, D, S and F, respectively. The first term of the sharp group would thus be $N/(1+S)^2$ and similarly $N/(4+D)^2$ would be the second term of the diffuse series. These are terms, not lines. They are universally represented in an abbreviated form by the expressions $(1S)$, $(2D)$, and so on. To get the complete set of terms m, for S, is given all integral values from 1 up, for P all values from 2 up, for D all values from 3 up, and for F all values from 4 up. The frequencies of the lines making up the series of lines are given by taking differences of terms as follows:

Principal series	$\nu_P = (1S) - (mP)$
Diffuse series	$\nu_D = (2P) - (mD)$
Sharp series	$\nu_S = (2P) - (mS)$
Fundamental series	$\nu_F = (3D) - (mF)$

where the variable integer in the second part has always for its lowest value one more than the fixed integer in the first part.

These formulas actually predicted the frequencies observed experimentally, although at the time of their formulation it could not be explained why this should be so. The terms used in the formulas are frequencies which, by the use of the quantum relation, $W = h\nu$, can be converted into energy expressions. It is apparent that under the Bohr theory these terms can be taken to

FIG. 1.



Sodium Spectrum

represent the energies of particular orbital motions and that the formulas just written, known since 1896, can be taken to be equivalent to the Bohr formula $h\nu = W_2 - W_1$. We are therefore enabled to apply a definite meaning to terms like $2P$ or $1S$ or $3D$ as representing a particular possible orbit with a specific calculable energy. The orbit $1S$ always represents the condition of least energy, that is to say, it is the outermost occupied orbit of the normal or unstimulated atom.

Fig. 1, which represents the possible orbits of the sodium atom, will serve to illustrate these points. The centre of the atom lies well to the right of the figure. The outermost orbit occupied in the unstimulated atom is $1s$. The vertical lines parallel to $1s$ give the energy levels which may be occupied by an electron

ejected through an energy absorption from the $1s$ level. The values of the energy differences of the orbits in ergs and therefore of the energy absorptions necessary to bring about the corresponding transitions are given above the arrows and, at the same time, the "terms" of the series formulas are expressed on the orbit lines by their proper frequency values. The fundamental formula $h\nu = W_2 - W_1$ being accepted, it is immediately apparent, when we observe in the figure the possible transitions of the displaced electrons as represented by the arrows, why differences of terms give frequencies of emitted lines. The transition $1s - 2p$ shows the mode of development of one of the well-known sodium lines. The $2p$ level is a doublet too close to be shown as such in the scale of the figure.

The identification of these energy levels with the spectrum terms, introducing an enormous simplification into spectroscopy, is clearly a procedure involving an assumption of the validity of Bohr's theory. Any proofs which can be adduced supporting this identification will consequently serve equally well to support the notions of atomic structure and of dynamics which are involved in the theory. We shall now pass on to a consideration of the experimental evidences which can be obtained bearing on the energy absorptions and emissions actually associated with the production of spectral lines.

Two generally useful methods have been found by which measurable quantities of energy can be imparted to atomic systems, first, by striking the atoms with electrons which have fallen through a known difference of electrical potential and have therefore a known energy, second, by allowing radiant energy of known frequency, made up of quanta of known magnitude, to fall on the atoms.

Let us examine the first of these methods, that of electron impact. This method, of all that have been devised, gives the most direct proof of the Bohr idea and the one most free from theoretical elements. A metallic filament heated to incandescence emits electrons. Let us suppose that we have such a filament in a vacuum and that electrons are coming through its surface with zero velocity. Let us place near the filament a metallic grid maintained at a positive potential, V, with reference to the filament. The electrons will fall to the grid and there will be done on each an amount of work eV since V, the potential difference, is the

work done per unit charge and e is the magnitude of the charge. If the potential difference is one volt, *i.e.*, 10^8 e.m.u. of potential difference, the energy of the electron on arriving at the grid will be $1.59 \times 10^{-20} \times 10^8 = 1.59 \times 10^{-12}$ ergs—for a potential drop of 20 volts it would be 3.18×10^{-11} ergs. Since the erg itself is, as measured by our senses, an exceedingly small unit, these energy quantities may seem insignificant; however, let us compare them with the energies associated according to the quantum theory with various frequencies of radiation. The frequencies of red light and of blue light are respectively 0.38×10^{15} and 0.76×10^{15}. Since the energy quantum, ε, of any frequency is given by $\varepsilon = h\nu$, where h is 6.55×10^{-27} ergs seconds, the quanta of these two radiations, red and blue, are seen to be 2.40×10^{-12} ergs and 4.98×10^{-12} ergs. These figures show that the potential energy developed by an electron in falling through even so small a potential drop as one volt is of the same order of magnitude as the quantum of red light. A simple calculation will show that a drop through 20 volts will give an energy equivalent to a quantum of radiation of wave-length 615 Å.*—very far down, indeed, in the extreme ultra-violet. Let us suppose that the space beyond the grid contains a certain number of atoms of a gas or vapor. The electrons which do not remain on the wires of the grid pass through and strike on the atoms. These atoms have electrons moving in concentric orbits about their nuclei and the electrons in the outermost orbit have, as we have already seen, a certain limited number of exterior orbits of greater energy in which it is possible for them to move. The atom is, according to these theories, incapable of absorbing any amount of energy excepting exactly such an amount as will throw an electron into one of the possible outer orbits. It happens, therefore, that when normal atoms are bombarded with electrons of gradually increasing velocity these will bounce off with undiminished energy until a certain critical velocity is reached at which they will suffer a definite loss of energy on impact. This loss of energy is the amount necessary to lift the atom-electron into its first exterior orbit; the equivalent potential is called the "resonance potential." With still further increases in velocity new impact losses will develop in successive steps until a final value is reached at which the atom becomes ionized—that is, appears

* Å. represents the Ångstrom unit of length, namely, 1×10^{-8} cm.

definitely with a net positive charge. This energy value is that necessary just to remove an electron completely from the field of force of the atom; the equivalent potential is called the "ionization potential." The successive critical velocities at which energy losses occur correspond to the absorption frequencies of the atom as observed optically—dynamically they correspond to the energy content of successively larger exterior orbits. If the electron is free after displacement to spring back into its original orbit the energy absorbed in going out will be given up in coming back as monochromatic radiation and will be contributed to the strength of some line in the spectrum of the gas. If the bombarding energy equals or exceeds the ionizing energy so that all the exterior orbits are being occupied and vacated in different atoms at the same time the total emission will comprise all of the lines of the absorption series. If the ejected electrons are dragged away by an exterior field so that reëntry into the atoms is impossible, ionization alone occurs without any emission of radiation.

The limiting energy of the striking electron which just lifts the atom-electron out of the atom is called, as we have stated, the ionization potential. The highest frequency line in the absorption spectrum of the element, the ultra-violet limit, corresponds to this ionization potential—the first line in that spectrum, that is the lowest frequency line, corresponds to the resonance potential or potential of the first inelastic impact. Having either of these potentials, or any of the intermediate potentials of inelastic impact, the frequencies of the corresponding spectrum lines are given by the simple formula $eV = h\nu$, in fundamental units, or by $V\ (\text{volts}) = \frac{12331}{\lambda(\text{Å})}$ in ordinary units.

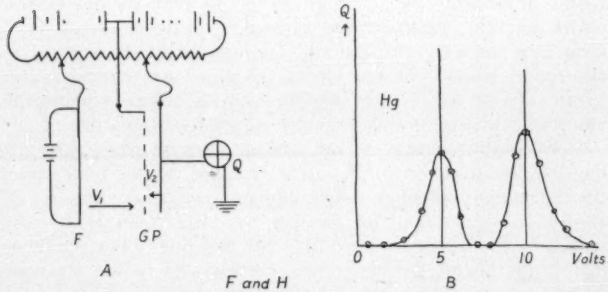
We have now before us the essential features of the phenomena of impact stimulation. The critical velocities of inelastic collision, including the ionization potential and the resonance potential as upper and lower limits, are seen to give us a direct measure of the energies of the atoms in certain of their stationary states. Studies of these velocities, therefore, furnish us with one of the most powerful means at our disposal for investigating the dynamics of atomic systems.

We shall next consider very briefly the methods involving electron impacts which have been used experimentally to determine these energy values. In the extensive literature of this subject a

variety of arrangements is described of which the two shown in Fig. 2 and Fig. 3 are typical.

Fig. 2 represents one of the original devices used by Franck and Hertz.[2] The electrons, developed from a hot wire, F, are accelerated to the grid, G, between which and the plate, P, a fixed retarding potential of a few volts is maintained. Suppose this retarding field to be three volts. As the accelerating potential, F to G, is gradually raised, no electrons can get to P until the driving voltage reaches three volts. The plate current registered by Q will then rise steadily as shown in the graph, B, until the energy

FIG. 2.

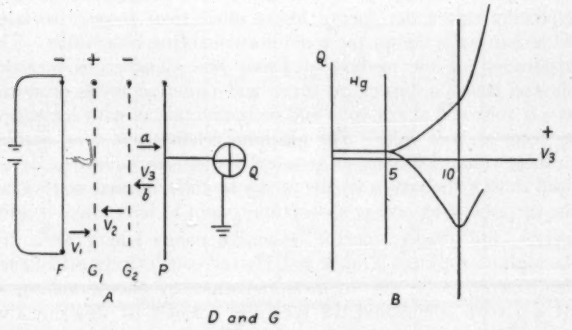


of the electrons striking the gas atoms in the plane of the grid is sufficient to lift atom-electrons from the outermost stable orbits of those atoms to the first possible exterior orbit. At this voltage inelastic impacts will occur between the electrons and the gas atoms. These inelastic impacts will reduce the velocity of the electrons to zero wherefore the current arriving at P will fall to zero and will remain at zero until the accelerating potential reaches a value three volts above the inelastic impact value. The plate current then rises as before until the electrons brought to rest in the first layer of inelastic impacts have, in falling forward from that layer, again acquired the critical energy necessary to throw the atoms into their first unstable state. At this point inelastic impacts will occur a second time and the plate current will again drop to zero and so on again if the accelerating voltage is lifted further. The potentials, F to G, at which the current in Q drops are clearly potentials of inelastic collision which may be either resonance

potentials or ionization potentials. The curve shown (Fig. 2*B*) is that for mercury vapor in which energy absorptions occur at five volt intervals.

Fig. 3 is a schematic diagram of an apparatus developed by Davis and Goucher [3] to differentiate resonance potentials and ionization potentials, something not readily done with the simpler apparatus of Franck and Hertz. Here a second grid, G_2, is introduced with arrangements whereby it may be made either positive or negative with reference to P. When the driving potential V_1 reaches a critical value inelastic impacts occur in the plane of G_1.

FIG. 3.



If these impacts are resonance impacts radiation only will be developed without the liberation of atom-electrons and the production of positive ions. This radiation, falling on both G_2 and P, will produce a photo-electric emission of electrons from whichever one is negative with reference to the other; consequently a current will flow in whichever direction the field V_3 may be established. Reversing this field at each voltage reading will give, therefore, a double curve, such as is shown at B (Fig. 3), leaving the voltage axis at the resonance potential. When, however, the impacts have sufficient energy to ionize the atoms at G_1, the liberated atom-electrons will be returned to G_1, by the field V_2, and, at the same time, the plus ions, that is, the positively charged atoms, will be carried across to G_2. If, now, V_3 is directed as represented by the arrow b (which refers to

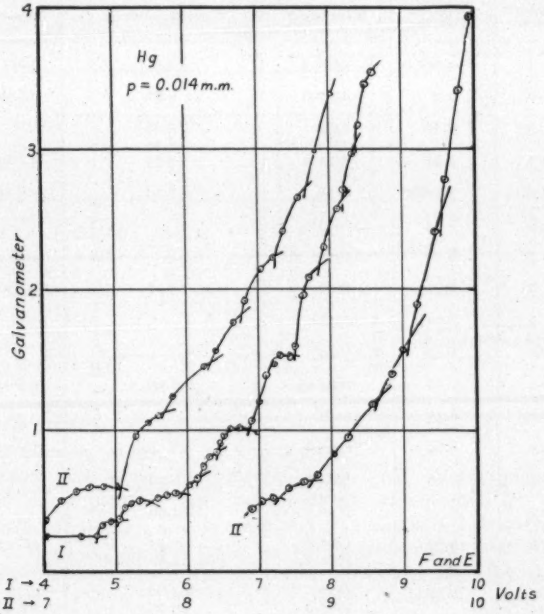
the motion of the electrons in the field) the plus ions will pass directly across to P and a positive current will be registered by Q. If, on the other hand, the field is set in the direction a but kept smaller than V_2, then the plus ions will still cross to P and a positive current will again be registered. These positive currents added to the photo-electric currents, which still reverse with V_3, give the upward breaks in the graph B which therefore clearly indicate the potential of ionization of the atoms.

In order to study the results obtained with such devices as those just described let us concentrate our attention on a single vapor, that of mercury—a vapor extremely suitable for such investigation because it is monatomic and because its atom is especially elastic, no energy losses other than those associated with changes in the atomic configurations being observable. The application of the method of Davis and Goucher to mercury showed inelastic impacts to occur and radiation to be produced at 4.9 volts and at 6.7 volts and inelastic impacts with ionization to occur at 10.2 volts. The quantum relation, $eV = h\nu$, applied to these voltages enables us to calculate that the radiations developed during the return of the atoms to their normal state after the corresponding energy absorptions ought to have wave-lengths 2537Å. and 1849Å. for the resonance points and 1188Å. for the ionization point. Franck and Hertz [4] conclusively established the presence of the first of these radiations by photographing it. At 4.9 volts stimulation the spectrum consists of this one line only. The other lines were not observed spectroscopically as they are absorbed by quartz. Evidence on the limiting short wave value of the spectrum, λ 1188, had previously been obtained, however, in an apparatus of a different character by Richardson and Bazzoni [5] who determined the maximum velocity of emission of the photo-electrons developed by radiation from a discharge in mercury vapor by curling them up into a circle of known radius in a magnetic field and found the length of the shortest waves from the arc to be not more than 1200 units and probably somewhat less—a result in good concordance with the value indicated by the impact method.

The early methods of investigation, such as those described above, could be depended upon to give the ionization potential and the resonance potential, that is, the point at which radiation is first developed and the point at which ionization occurs,

but they were apparently not capable of detecting all those intermediate energy absorptions which ought to be associated with the occupation of successive orbits below the ionization potential. In 1920 Franck and Einsporn [6] succeeded in getting results with a method in which these successive potentials could be separated

FIG. 4.



by noting, under carefully controlled conditions, the successive rises in the photo-electric current from an electrode exposed to the radiation from the discharge. The results obtained by them using mercury are shown in Fig. 4. The breaks in the curves, which are curves of photo-electric current, indicate the potentials at which new radiations appear. A total of eighteen successive energy steps between the resonance potential and the ionization potential were determined although the final values do not all

appear in the figure shown. The exact values are collected in the table (Fig. 5). Before the significance of the spectrum terms at the right of the table can be made apparent something must be said of the constitution of the mercury spectrum as determined

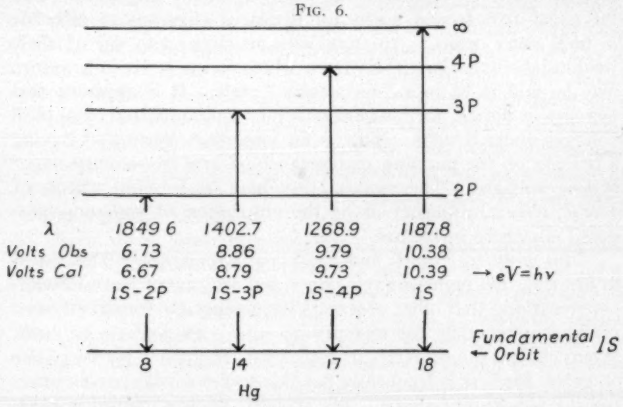
FIG. 5.

Number of Line.	Observed Voltage.	Wave-length.	Calculated Voltage.	Series-term.
1	4.68	2656.5	4.66	$1S-2p_3$
2	4.9	2537.0	4.86	$1S-2p_2$
3	5.32	2338	5.28	
		2313	5.34	
4	5.47	2270.6	5.43	$1S-2p_1$
5	5.76	2150	5.73	$2p_3$
6	6.04	(2043)		
7	6.30	(1958)		
8	6.73	1849.6	6.67	$1S-2P$
9	7.12	(1733)		
10	7.46	(1654)		
11	7.73	1603.93	7.69	$1S-1s$
12	8.35	(1446)		
13	8.64	1435.6	8.58	$1S-3p_2$
14	8.86	1402.7	8.79	$1S-3P$
		1400.0	8.81	$1S-3d_1$
15	9.37	2656.5	2×4.66	
16	9.60	1307.8	9.44	$1S-4p_2$
		2656.5	$4.66+4.86=9.52$	
17	9.79	2537	2×4.86	
		1268.9	9.73	$1S-4P$
18	10.38	1187.8	10.39	$1S$

by the spectroscopists. This spectrum is a complex one consisting of a set of singlets (single lines) and of a set of triplets which form combination series with each other. The principal series of singlets of the normal atom is, as usual, $1S-mP$ where m has all values from 2 up, S equals 84178.5 and P equals 30112.8. When m is made 2 in this formula the first line of the series is

found to be 1849.6Å.—the limiting line ($m = \infty$) is $1S$ which has a wave-length 1188Å. This is the absorption series of the normal atom of which we have already spoken developed by electrons falling back from the exterior unstable orbits into which they have been thrown from the fundamental orbit. Fig. 6 shows the first four lines of this series. The check of Franck and

FIG. 6.



Einsporn's experimental results with those calculated from the series formula is seen to be excellent.

From the same fundamental orbit, $1S$, a combination series of triplets is also developed as represented by the formula $1S - mp_{1,2 \text{ or } 3}$ ($p_1 = 40138.3$, $p_2 = 44768.9$, $p_3 = 46536.2$ —the small letters referring to the triplet orbits, the large letters to the singlet orbits). Now although only the middle term, $1S - mp_2$, of each of these triplets is observed in emission and absorption by optical methods nevertheless an examination of the results of Franck and Einsporn shows a break at 4.68 volts and one at 5.47 volts corresponding exactly to radiation of 2656.5Å. and 2270.6Å., respectively, the two outside lines of the first triplet of this series. Since these outside lines are unknown in the optical spectra it has been concluded that electrons cannot ordinarily fall from these orbits to the fundamental orbit. In this connection we note

the break at 5.76 volts which indicates an inelastic impact supplying exactly the energy necessary to throw the electron from the $2p_3$ orbit entirely out of the atom, giving in two steps the total energy, 10.39 volts, necessary for ionization. To give opportunity for the two successive impacts on the same atom necessitated by this type of ionization we must suppose that the electron remains in the $2p_3$ orbit for a longer time than the usual 10^{-8} second given for displaced electrons to circulate in their outer orbits. An atom with an electron in one of these pseudostable exterior orbits from which it cannot readily return may be said to be in a "metastable" state. It is apparent that mercury in the $2p_3$ form of metastability can be ionized by applied voltages under 6 volts. This is an important conclusion having a bearing on the puzzling maintenance of arcs in mercury vapor at low voltages. The metastability may be brought about, of course, either by impact or by the absorption of radiation produced elsewhere in the arc.

This work of Franck and Einsporn is remarkably well suited to illustrate the points of this paper, but we cannot leave it without remarking that other observers have generally found only two resonance potentials for mercury—$\nu = 1S - 2p_2$ and $\nu = 1S - 2P$. When one has a long series of somewhat irregularly placed points on graph paper it is frequently possible to get partial curves intersecting almost anywhere. The results of less skilled experimenters who have followed in Franck and Einsporn's steps in recent months demand critical scrutiny.

Two other series, $1S - ms$ and $1S - md$, arise from the $1S$ orbit of mercury. An examination of the eighteen breaks in the curve of Fig. 4 now shows all of the lines terminating in the $1S$ orbit to be accounted for with a number left over. Whatever may be thought of the flexibility of the conclusions drawn from this particular research it cannot be denied that work of this kind has furnished valid evidence of the existence of energy absorptions corresponding to the occupation of successively enlarged stationary states by the electrons of stimulated atoms.

Although the mercury atom is, as has been said, an easy one with which to experiment, its structure is nevertheless complex. With an atomic number of 80 its shell construction, according to Bohr's latest theory,[7] is (nucleus + 80) electron shells -2, -8, -18, -32, -18, -2. Its spectrum contains 177 lines. It must be

remembered, however, that all of these lines of the optical spectrum are developed by the two outermost electrons being to a large extent unaffected by the complex interior of the atom. The interior shells are, as is well known, involved in the production of X-ray spectra lines, the quanta of which are very large and the frequencies correspondingly high.

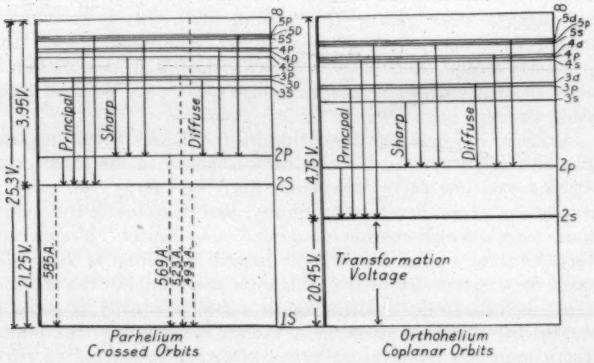
Let us now turn our attention to helium—that gas which of all others on account of the simplicity of its structure would seem to offer the most promise of successful investigation of its interior dynamics. Although hydrogen has a simpler atom than helium yet its tendency to form molecules renders it in experimental work less easy to deal with. The helium atom, being structurally simple, (nucleus + 2) electron shell −2, one might expect that its secrets would soon have been penetrated but, as a matter of fact, for many years it has furnished physicists with an interesting puzzle.

Bohr in his first representation of the helium atom supposed the two electrons to be diametrically opposite in the same orbit. On this basis he easily calculated that the energy necessary to remove one of the electrons to infinity, that is, to ionize the neutral atom, corresponded to that of a 28.8 volt impact. Franck and Hertz [8] found a point of inelastic impact in helium at 20.5 volts which they interpreted as the ionization potential, but the presence of a third electrode in their device made it equally possible to ascribe the observed effect to a radiation potential—the photo-electric emission from the collecting electrode producing an effect indistinguishable from that due to plus ions developed in ionization. The first determination of the helium ionization point in a two-electrode device was made by Bazzoni [9] in 1916. The result showed unmistakable ionization close to 20 volts. About the same time Richardson and Bazzoni showed by a photo-electric measurement that there is radiation in the helium arc of a wave-length which at the lowest value must correspond to impacts of about 26 volts energy indicating that true ionization cannot take place below that voltage. These facts, together with others collected in the same series of experiments, led Richardson and Bazzoni [10] to formulate a theory, published in 1916, that impact ionization is not a simple phenomenon but that it is facilitated by radiation absorption so that ionization can result from impacts on atoms in an abnormal condition caused by the absorption of

radiation generated in other atoms in consequence of electron impact. The ionization potential might therefore be shifted back to the first resonance potential as its limiting value. This idea has been developed mathematically during the past year by K. T. Compton [11] and has been found adequate to explain the observed effects.

The spectrum of helium is very peculiar being divided cleanly into two independent sets of series, principal, sharp, diffuse, and so on, exactly as if the gas were made up of two different kinds

FIG. 7.



of atoms. This implication is so definite that formerly two kinds of helium were supposed to co-exist, orthohelium and parhelium, the first being distinguished by a spectrum of double lines, the second by a spectrum of single lines. The energy relations of these series are shown in Fig. 7.[12] The optical spectra, represented by the solid arrows in the figure, are seen to stop short of the innermost orbit. None of the lines so shown are absorption lines indicating that of the transitions represented, none terminate in the normal atomic configuration. The lines, consequently, whose frequency numbers would enable us directly to calculate the ionization potential do not appear in the ordinary optical spectra. They lie in the extreme ultra-violet and are being investigated at the present time by Lyman with his vacuum spectrograph. These ultra-violet lines corresponding to transitions

from and back to the fundamental $1S$ orbit constitute the absorption spectrum of helium. They are shown in Fig. 7 by dotted arrows. The results published by Lyman [13] last summer do not fit in well with the numerical details about to be stated nor with the numbers given in Fig. 7. The explanation of these discrepancies will be pointed out later. The facts most generally accepted at the present time and represented in Fig. 7 are these—that the normal atom is the $1S$ state of parhelium, that in this atom, called the crossed-orbit atom, the two electrons revolve in very slightly elliptical orbits inclined at an angle of 120 degrees to each other; that orthohelium is a metastable form, the lowest possible energy state being the $2s$ orbit which can be reached from the normal state only by an energy absorption from impact or ultra-violet radiation corresponding to 20.45 volts. This is called "the transformation voltage." In this metastable state the two electrons revolve in coplanar orbits one outside the other. For this reason orthohelium is frequently called "coplanar" helium. This $2s$ state, possessing as it does considerable stability, serves as the fundamental orbit for the optical series of orthohelium. An energy absorption of 21.25 volts by the normal atom will give us parhelium in the $2S$ state which also possesses some stability, though not as much as the $2s$ state, and is the fundamental orbit for the optical series of parhelium. The energy necessary to throw the electron into its $2s$ or $2S$ orbit, respectively 20.45 and 21.25 volts, plus that necessary to remove the electron from those orbits to infinity, respectively 4.75 and 3.95 volts, is taken to be the ionization energy of the normal atom. It will be seen that ionization is possible under this scheme with any electron bombardment energies greater than 20.45 volts but that true ionization by a single impact on a normal atom ought to require 25.3 volts.

It must be admitted that the experimental evidence for any notion as to the true fundamental orbit being the $1S$ state of parhelium is meagre and not too concordant but the results of Franck and Knipping,[14] Franck and Reiche,[15] Horton and Davies [16] and Compton [17] have united in establishing the existence of a resonance potential at 20.5 volts, of another resonance potential at 21.3 volts and of an ionization potential at 25.3 volts thus accounting for visible spectral lines as exemplified in the figure. Of these potentials the first, 20.5 volts, is the transformation voltage which ought not to cause any radiation since the

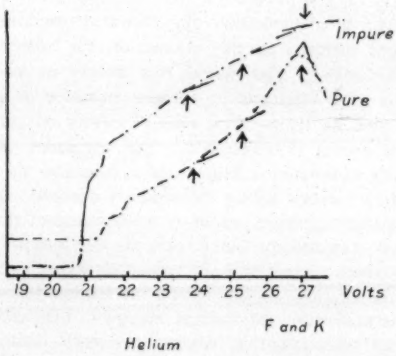
atom is thereby thrown into a metastable form from which it cannot return directly to the normal state. The second, 21.3 volts, corresponds to a radiation of wave-length 585Å. and the third, the ionization potential 25.3 volts, to a radiation of wave-length 493Å. which, therefore, ought to be the ultra-violet limit of the helium spectrum. Other less firmly established inelastic impact potentials have been observed at 21.9 volts (corresponding wave-length 569Å., $1S-2P$) and 23.6 volts (corresponding wave-length 523Å., $1S-3P$).

Lyman's results of last summer, referred to above, establish however by direct spectroscopic observation the presence of lines of wave-lengths 515.7Å. (23.92 volts), 522.3Å. (23.62 volts), 537.1Å. (22.97 volts) 584.4Å. (21.12 volts) and, less certainly, 600.5Å. (20.55 volts). The calculated limit of this series is wave-length 502Å. (giving 24.6 volts as the ionization potential). The publication of Lyman's results has led Franck [18] to reëxamine Franck and Knipping's values and to correct their voltmeter readings by 0.7 volt thus giving an exact concordance between their impact values (suitably corrected) and Lyman's spectroscopic observation. A concordance so obtained is not very convincing and we can only conclude that the impact potentials of helium require further study. This need is the more apparent when we note that the only published calculation (Van Vleck's [19]) of the ionization potential of crossed-orbit helium gives 20.7 volts and not 24 or 25 volts as the observations above quoted would seem to demand.

Fig. 8 will serve as an example of some of the experimental results of the impact investigations. This figure gives the results of certain studies made by Franck and Knipping on the radiation developed from helium. The significant breaks which support the theory are indicated by arrows as otherwise they might be overlooked. There are, however, curves made by other methods which give more unmistakable break points. This figure is used in order to bring out the fact that in absolutely pure gas the 20.45 radiation corresponding to the breakdown of the metastable coplanar orthohelium is absent, indicating, apparently, that orthohelium once formed by impact can return to parhelium only in the presence of some impurity. This may be

explained by noting that $2S$ orthohelium is structurally like lithium, having a single electron in an exterior orbit, and ought, therefore, to possess a definite chemical reactivity. This means that in the presence of a molecule with which the atom might react, strong molecular electrical fields must be developed. It is the presence of these strong fields which renders possible the return of the coplanar atom formed by a 20.5 volt impact to the normal crossed-orbit form liberating the radiation shown by the rise in the curve in the diagram. In the absence of impur-

FIG. 8.



ity the extra electrical field is also absent and this return cannot take place; hence the absence of 20.5 volt radiation in the pure gas. That the interchange from the orthohelium to the parhelium form should be possible only in the strong field is rendered plausible by a mathematical development of the Bohr theory into which we cannot enter here.

It is interesting to note that the probable chemical activity of metastable helium may explain the progressive absorption of helium in the metal films inside vacuum tubes.

In summing up we may say that impact investigations have explained in a general way the optical series of helium and that unquestionably helium atoms possess above their fundamental orbits certain metastable states with different electron configura-

tions. We are not yet justified, however, in saying anything definite about the energy content or real arrangment of the fundamental orbit. The calculations which Bohr has promised to publish bearing on this matter will furnish fresh material for the experimentalists to work on.

It is impossible within the limits of this paper to say anything about the interesting, if somewhat complicated, results which impact methods have given when applied to polyatomic molecules. In these cases the energies of dissociation must be considered in connection with the ionization and resonance energies. When this subject is fully worked out it may be expected to throw light on the mechanism of monomolecular chemical reactions.

We might mention in this connection the recent work of Franck and Cario [20] who found that atoms in a stimulated state, that is with electrons in exterior unstable or metastable orbits, can give up their excess energy merely on contact with unstimulated atoms or molecules. The particular observation was that such stimulated mercury atoms dissociate the hydrogen molecule into its atoms during the ordinary contacts which occur due to molecular agitation. This is neither impact transference nor radiation transference but is nevertheless a type of energy interchange which we might easily expect to occur.

It now remains to consider briefly the stimulation of spectral lines by the absorption of radiant energy. The atom can be stimulated to emit radiation whenever certain definite energy quantities are imparted to it exactly sufficient to lift some of its electrons into an exterior possible orbit. It does not matter how the energy is supplied. If the gas is subjected to radiation instead of to electron bombardment an emission will occur if the quantum $h\nu$ of the incident radiation has the critical magnitude necessary to lift an electron into an exterior orbit. This critical frequency, ν, is referred to as the resonance radiation of the atom. The absorbed radiation of frequency ν is reëmitted with the same frequency. This so-called resonance effect was demonstrated by Wood [21] who showed that sodium light passed through sodium vapor was capable of stimulating the emission of the D lines. The most interesting and significant of recent researches in this field is by Fuchtbauer.[22] Fuchtbauer made use of a quartz mercury lamp of novel construction. A cross-section of this

lamp is shown in Fig. 9. A discharge was maintained in the annular tube *A* by the usual methods. The space *B* contained cold mercury vapor. The chamber *C* was filled with liquid mercury and acted as a cylindrical reflector to concentrate the radiation from *A* into *B*. The radiations stimulated in the cold vapor in *B* were then photographed through a plate at the end of the device. The wall of *B* was of such thickness that the strong ultra-violet line, λ 1845, was thought to be entirely absorbed so that the bulk of the short radiation received in *B* must have come from the next strong line, λ 2537. The radiation stimulated in the cold vapor by this absorption of λ 2537 was found to consist of over thirty measurable lines. The probable way in which

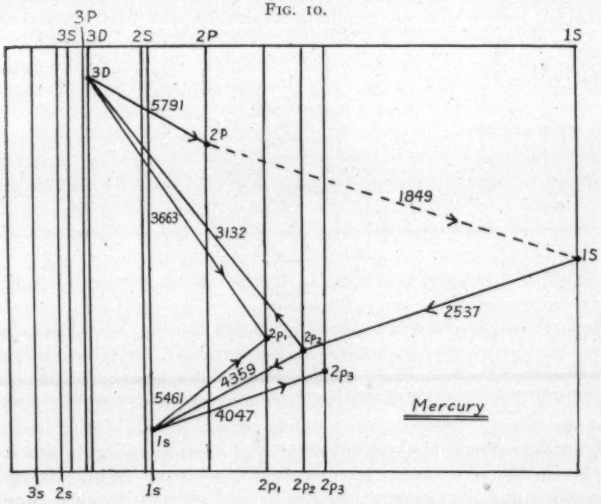
FIG. 9.

these radiations were developed is shown in Fig. 10. Here the spectral terms corresponding to the various energy levels are represented by dots, their relative magnitudes being proportional to their distances from the atom centre which lies to the right of the figure. Some of the possible transitions are shown in the figure by arrows, absorptions of energy corresponding to transitions to the left, emissions to transitions to the right. It will be noted that the primary absorption of λ 2537 throws the atom into the state where it may finally radiate λ 1845, a radiation which has a higher energy quantum than the original stimulating radiation. Study of this investigation throws much light on the complex interchanges which go on in arc discharges tending to alter in various ways the normal stability of the atomic systems. The facts thus brought out are of such significance that further study of them is desirable. It ought to be more definitely established that the stimulating light contains no wave-lengths shorter than λ 2537.

Conditions such as we have in Fuchtbauer's mercury column account for the persistence in arcs of atoms in stimulated states

for appreciable lengths of time (of the order of hundredths of a second) as observed by a number of experimenters. Again, whenever there is metastability there will be, by definition, a persistence of stimulated states over a certain time and therefore a persistence of the emission of radiation after the cessation of the original cause. The active nitrogen of the chemist, one of the principal characteristics of which is the ability to retain lumi-

FIG. 10.

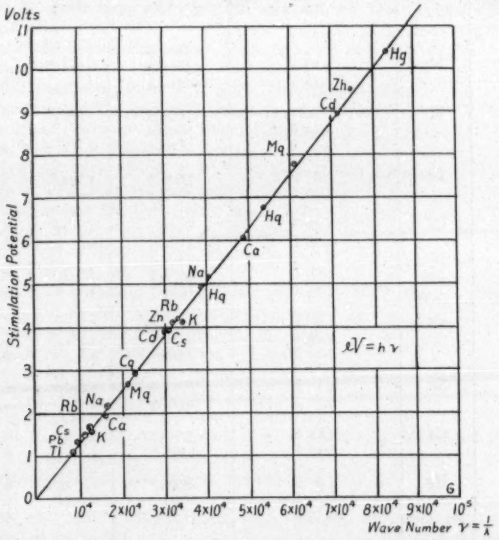


nescence after the cessation of a discharge passed through it, is thus seen to be possibly a metastable form of nitrogen. Swelled up atoms with occupied exterior orbits possessing as they do a less stability will in most cases possess a greater chemical reactivity than the normal forms.

In concluding this incomplete survey of ionization and resonance phenomena it will be useful to show that the measurements, which have now been carried into most of the columns of the periodic table, possess, on the whole, considerable precision. It is easily seen that when an ionization potential can be definitely associated with a corresponding spectroscopically observed line

the relation $eV = h\nu$, if plotted with the spectroscopic ν against the electrically measured energy eV necessary to stimulate it, will give a straight line the slope of which is Planck's constant h. Fig. 11 gives such a graph. An idea can be obtained from the figure, which is not complete to date, of the range over which the measurements have been extended. The data used in the graph

FIG. 11.



is tabulated in Fig. 12. The average value of the slope is seen to be 6.56×10^{-27} ergs seconds while the value for h at the present time accepted as best, determined by seven independent methods, is 6.554×10^{-27}. This agreement is sufficiently good to establish the methods of impact measurements among the more dependable of experimental physics. A large percentage of the values here tabulated were determined by Foote and Mohler and their associates [23] at the Bureau of Standards.

I have endeavored in this paper to show how Bohr's theory is related to the series formulas representing optical spectra and

to give a sufficient number of illustrations to make clear that experimental measurements have uniformly combined to prove the validity of the interrelation. I have endeavored, furthermore, to show that atoms and consequently molecules in a bath of

FIG. 12.

Periodic Group.	Element.	Potential in Volts. R — Radiation. I — Ionization.	Wave-length Å.	Series-term.	h
			5889.9		
1	Na	2.12 R	5895.9	$1S$–$2P$	6.63
		5.13 I	2912.6	$1S$	6.57
	K		7664.9	$1S$–$2P$	6.32
		1.55 R	7699.2		
		4.1 I	2856.7	$1S$	6.22
	Rb	1.6 R	7800.3	$1S$–$2P$	6.61
		4.16 I	2968.4	$1S$	6.54
	Cs	1.48 R	8521	$1S$–$2P$	6.69
		3.88 I	3184.2	$1S$	6.58
2	Mg	2.65 R	4571.4	$1S$–$2p$	6.43
		7.75 I	1621.7	$1S$	6.67
	Ca	1.9 R	6122.5	$1S$–$2p$	6.54
		2.85 R	4226.9	$1S$–$2P$	6.38
		6.01 I	2027	$1S$	6.45
	Zn	4.1 R	3075.9	$1S$–$2p$	6.70
		9.5 I	1319.9	$1S$	6.66
	Cd	3.88 R	3260.17	$1S$–$2p$	6.71
		8.92 I	1378.69	$1S$	6.53
	Hg	4.9 R	2536.7	$1S$–$2p$	6.60
		6.73 R	1849	$1S$–$2P$	6.60
		10.35 I	1187.99	$1S$	6.53
3	Tl	1.07 R	11513	$1S$–$2p$	6.53
		7.3 I			
4	Pb	1.26 R	10291		6.87
		7.93 I			
Accepted "best" value from seven independent methods 6.554×10^{-27}				Average	6.56×10^{-27}

radiation, however produced, are powerfully affected and frequently fundamentally altered in their dynamic constitution, being thrown into metastable forms in which their reactivities are often intensified or even changed in nature. Looking forward it

certainly seems that further advances in the fields here under discussion can be depended upon to furnish solutions for some of the basal problems of atomic and molecular interactions which have always underlaid the science of chemistry but which have heretofore eluded investigation.

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[22] Fuchtbauer: *Phys. ZS.*, **21**, 635, 1920.
[23] Foote, Mohler and associates: *Phys. Rev.*, **11**, 486, 1918; **13**, 59, 156, 1919; **15**, 322, 1920; *Phil. Mag.*, **42**, 1002, 1921; **43**, 659, 1922, etc. "Origin of Spectra," 1922.

Action of Natural Waters on Lead. JOHN C. THRESH (*Analyst*, 1922, **47**, 459–468, 500–505) has studied the corrosive action of natural waters on metallic lead. Pure water has no action on lead; but action occurs in the presence of oxygen; plumbic oxide or hydroxide is then formed and remains in solution in a colloidal condition. Certain organic compounds, which occur in moorland waters, tend to retard the oxidation of the lead, but also tend to retain in solution any lead which is dissolved. The corrosion or oxidation is retarded by the presence of silicates, but not by the presence of sulphates, chlorides, carbonates, bicarbonates, or an excess of carbonic acid. J. S. H.

The Electrical Structure of Matter. SIR ERNEST RUTHERFORD. (*Science*, Sept. 21, 1923.)—This is the presidential address before the British Association for the Advancement of Science at its meeting in September, 1923, at Liverpool. In these twelve pages is summed up with admirable clarity the present condition of our knowledge of the structure of the atom. It is to this article that he must turn who desires to inform himself of the state of affairs on this frontier of scientific investigation. Of much that he relates the eminent author might well have added "quorum pars magna fui," yet he keeps himself in the background.

To counteract some popular but too enthusiastic hopes, the following may be quoted: "It is well known that the total evolution of energy during the complete disintegration of one gram of radium is many millions of times greater than in the complete combustion of an equal weight of coal. . . . This possibility of obtaining new and cheap sources of energy for practical purposes was naturally an alluring prospect to the lay and scientific man alike. . . . With increase in our knowledge of atomic structure there has been a gradual change of our point of view on this important question, and there is by no means the same certainty to-day as a decade ago that the atoms of an element contain hidden stores of energy."

G. F. S.

Sodium Sulphate.—ROGER C. WELLS is the author of a monograph on "Sodium Sulphate: Its Sources and Uses" (*U. S. Geol. Survey Bull. No. 717*, 43 pp., 1923). This salt occurs in nature in the anhydrous condition as Thenhardite, as the decahydrate or Glauber's salt (mirabilite), and as a constituent of several complex minerals, chiefly double sulphates. In addition to the natural product, sodium sulphate also enters commerce as salt cake and niter cake which are by-products of the manufacture of hydrochloric acid and nitric acid, respectively. Niter cake also contains sodium acid sulphate and pyrosulphate. Natural deposits of sodium sulphate occur in at least eleven states west of the Mississippi River, in Canada, Mexico, and the Argentine, also in the eastern hemisphere. Sodium sulphate is used chiefly in the manufacture of wood pulp, glass, and sodium sulphide, to a lesser extent in dyeing, tanning, ore flotation, and medicine.

J. S. H.

Dakin Solution.—Dakin solution is a buffered aqueous solution of sodium hypobromite, and is used as a bactericide. When prepared from chloride of lime and a mixture of carbonate and bicarbonate of sodium, Dakin solution frequently has a pink color. J. HOLDEN (*U. S. Naval Med. Bull.*, 1923, **19**, 156–157) states that this pink color is due to the presence of sodium permanganate; manganese may be present in the chloride of lime as calcium manganate, and is converted into sodium permanganate in the preparation of the Dakin solution. The presence of permanganate is believed to be desirable rather than objectionable.

J. S. H.

STUDIES IN PHOTOGRAPHIC SENSITIVITY.*

III.

TOPOCHEMISTRY OF DEVELOPMENT AND SENSITIZING NUCLEI.

BY

S. E. SHEPPARD, E. P. WIGHTMAN and A. P. H. TRIVELLI.

Research Laboratory, Eastman Kodak Company.

THE term "topochemistry," in reference to the silver halide grains of photographic emulsions, embraces effects which can be related to the *position* of a component in the grain, and refers principally to distinctions between effects on the outside (surface) and the inside of the grain.

These distinctions were sufficient when the crystalline character and structure of the grain were less precisely known; at the present time, not only is the crystallographic structure accurately known,[1] but statistical data on the sizes, shapes, and orientations of the grains in emulsions are being rapidly obtained.[2] Consequently, a "topochemical" reference to a silver halide grain may well require much greater precision of statement. Surface distribution, for example, covers both edge and plane faces (on polyhedra) and does not differentiate between cubic and octahedral faces. But these finer distinctions will not be considered until necessary, and the term "topochemical" will be used in the broad sense unless otherwise specified. While many workers have at one time or another made use of "topochemical" considerations in dealing with the photographic emulsion, it is to Lüppo-Cramer that we owe the most numerous, as also the most varied and ingenious, applications of this conception.[3]

Although in certain cases, we may disagree more or less con-

* Communicated by Dr. C. E. K. Mees, Director of Laboratory and Associate Editor of this JOURNAL. Published as Communication No. 190 from the Research Laboratory of the Eastman Kodak Company.

[1] A. P. H. Trivelli and S. E. Sheppard, "The Silver Bromide Grain of Photographic Emulsions," Eastman Kodak Company, Rochester, N. Y.

[3] *Cf.* E. P. Wightman, A. P. H. Trivelli and S. E. Sheppard, *J. Phys. Chem.*, **27**, 1, 141, 466 (1923); JOUR. FRANK. INST., **194**, 485 (1922).

[2] As we shall have occasion to refer repeatedly to this author's publications on the subject, we shall leave references to their specific occasions.

siderably with Lüppo-Cramer's contentions, we should like to acknowledge the wealth of new facts which he has brought to light and the fertility of thought which he has applied to their explanation.

I. EFFECT OF IODIDE AND NUCLEUS EXPOSURE.

The introduction of iodide into the silver bromide grain has been shown to lead to a considerable number of distinct and remarkable effects.[4] In explanation of effects produced by:

1. Presence of silver iodide in the emulsion.
2. Treatment of silver bromide emulsions previous to exposure, resulting in:
   (*a*) Increase of "sensitivity" for physical development.
   (*b*) Red sensitizing for chemical development.[5]
3. Treatment after exposure, prior to development, or incorporation in the developer, resulting in:
   (*a*) Acceleration of development for certain developers (Lainer effect).
   (*b*) "Fogging" with physical development.

Lüppo-Cramer has introduced and developed the hypothesis of "Keimblosslegung," which we shall refer to as "nucleus exposure."

At its simplest, the conception is that certain reagents interacting with silver halide grains may mechanically disintegrate them so that occluded silver nuclei are exposed, and become reactive. This conception was applied particularly to the various "iodide effects" instanced above. But in order to cover cases where the iodide is incorporated early in the emulsion, the hypothesis has to be modified. Lüppo-Cramer has pointed out, quite correctly, that its effect, *whatever the mechanism*, will itself depend upon its distribution in the grain. This can vary from a homogeneous solid solution to a purely superficial coating. In order to extend his hypothesis to cover cases where the early presence of iodide in the grain produces effects similar to those obtained by its subsequent introduction, Lüppo-Cramer has introduced an auxiliary hypothesis of a very general character. This is the hypothesis of "facilitation of formation of free silver nuclei [germs] in consequence of the presence of silver iodide."

[4] *Cf.* Lüppo-Cramer, "Kolloid Chemie u. Photographie," 2nd Ed.
[5] F. F. Renwick, *Phot. J.*, **61**, 12 (1921).

Although this was introduced as auxiliary to the earlier conception of mechanical "nucleus exposure," it appears that considerably different forces are involved, and that the ground is rather cut away under the mechanical concept. However, it is obvious that for effects produced when iodide is present in the emulsion—the mechanical disintegration hypothesis is not *sufficient.* Hence the query arises, is it *necessary* to explain the type (2) effects? Lüppo-Cramer's auxiliary hypothesis does not suggest a definite mechanism.

In a paper [6] on the Lainer effect, the acceleration of development by iodide (on prebathing, or in the developer), one of the writers proposed a considerably different explanation. Namely, adsorption of reducing agents to the iodized grain, increasing the potential at the surface. In particular, this appeared more satisfactory in regard to the selective character of the Lainer effect, which is only shown with certain low potential developers.

This explanation does not seem entirely adequate in the case of the facilitation of "physical" development fog, and chemical "fog" (specific to certain developers and iodide concentrations) described in other papers.[7] Here it was suggested that the silver iodide brought together both nascent silver and reducer. In the case of "physical" development [8] we have moreover the known tendency of silver iodide to adsorb silver ions. This tendency increases along the series,

$$AgCl \longrightarrow AgBr \longrightarrow AgI$$

corresponding with the increased peptization and solution of the silver halides in solutions of silver salts.

If we may speak then of a general contact catalytic effect [9] of silver iodide in photographic emulsions it appears reasonable that the adsorptive capacity of silver iodide must be borne in mind. This appears to have been neglected by Lüppo-Cramer in developing his general thesis of "facilitation, etc." Thus in his article on "The Characteristics of the Silver Iodide Image" [10] he notes

[6] S. E. Sheppard and G. Meyer, *J. Am. Chem. Soc.*, **42**, 689 (1920).
[7] S. E. Sheppard, "Effect of Iodides, etc.," *Phot. J.*, **46**, 88 (1922).
[8] *Cf.* Lottermoser, *J. prakt. Chem.*, **73**, 374 (1906).
[9] Rather of a "promoter" than direct type.
[10] *Phot. Korr.*, **50**, 561 (1913).

that a pure AgI emulsion—supposed free from reduction nuclei [11] —when compared with a pure AgBr emulsion as similar as possible—gave on *physical development* before fixation somewhat higher sensitivity, and greater density. After fixation, the silver from the AgI emulsion was easily rubbed off. But if *physical development after fixation* was used, the AgBr emulsion showed the higher sensitivity (20° C. J. compared with 12° C. J.) and density. From this he concludes that the actual photochemical decomposition of the AgBr was greater, giving more nuclear material, but that AgI furnishes nuclei of greater activity in respect of the "typical grain surface development" operative in physical development.

In explanation of this he assumes that the nuclei are "obviously much more exposed in the first case, while in the silver bromide they are firmly enclosed and inactivated." Hence he concludes that we cannot speak of a greater "light sensitivity of silver iodide, but only of a greater tendency to the formation of active nuclei for physical development."

As against this, it would seem evident that the well-known high adsorption of *silver ions* to AgI affords an explanation of a considerable part of this result. The more rapid reduction at the surface would result in a less coherent deposit, as well as the higher apparent sensitivity. After removal of silver halide the situation would be changed—in fact, the residual silver nuclei might actually be more firmly occluded in the residual latent image after fixation. In any event, it will be observed that in the foregoing the function of the AgI is necessarily attributed to a *predisposing influence*, not to any actual mechanical disintegration.[12]

As further evidence of the adsorption factor, some results of A. Steigmann [13] may be cited. In a paper on the reduction of sodium silver thiosulphate by sodium hyposulphite [14] he states that the initial induction period, when no silver is precipitated,

[11] "Keimfrei."

[12] In the case cited, Lüppo-Cramer finds that the nuclei on AgBr grains are more than on AgI after fixation. Yet elsewhere he states that when an AgBr plate is treated with KI before fixation, the opposite effect was observed, *i.e.*, more active nuclei after fixation than with plain AgBr.

[13] *Koll. Zeits.*, **28**, 29 (1921).

[14] $NaHSO_2$, often termed hydrosulphite.

may be overcome, by inoculating the solution either with colloid silver [15] or with *silver iodide*. The catalytic effect of the latter Steigmann attributes to a relatively easier reducibility compared with the complex silver thiosulphate anion—although the latter furnishes silver freely once the induction period is passed! In his words, "In this case silver nuclei or nuclear complexes are formed from AgI before they can arise out of the difficultly reducible sodium silver thiosulphate in excess thiosulphate. Exactly the same results are obtained as on addition of (silver) nuclei in an inoculating solution. The nuclei formed from the AgI, which act as 'seed crystals' do not permit any supersaturation to occur in the further course of the reaction by which new nuclei could be formed."

First it seems contradictory to ascribe greater reducibility to the AgI than to the silver thiosulphate complex, when at the same time admitting that the latter can furnish a considerably supersaturated solution of metallic silver in the absence of colloid silver nuclei or silver iodide. We have a case of heterogeneous catalysis, in which the specific effect of the silver iodide is shown. In view of similar results in chemical reduction of silver bromide by one of the authors,[16] a more probable explanation seems to be that here the AgI anchors to it both the reducer and the reducible silver anion. Further, an orientation of the complex silver anion could occur leading to a loosening of the silver, this favoring reduction. For AgI strongly adsorbs silver ions, and hence will favor displacement of the equilibrium

$$\left[Ag\,(S_2O_3)_2\right]^{=} \rightleftarrows Ag^{+} + 2\left[S_2O_3\right]^{=}$$

at its surface. Again, in any case, it is a predisposing influence of the AgI which must be called into account here, and not the "mechanical germ" exposure.

II. THE LAINER EFFECT.

In the cases just discussed, there can be no question of mechanical "Keimblosslegung." The Lainer effect consists in the acceleration of chemical development of AgBr by treatment

[15] *Cf.* "Inoculation of Silver Sulphite Solutions in Excess Sulphite," S. E. Sheppard, *Phot. J.*, **59**, 136 (1919).

[16] S. E. Sheppard, "Action of Iodides and Cyanides, etc.," *loc. cit.*

of the plate prior to development with dilute KI solution, or addition of this to the developer. It has been discussed fully by one of the authors elsewhere.[17] The effect is limited to certain low potential developers, such as hydroquinone. As was pointed out in the paper referred to, it is a weak point of the mechanical explanation of this effect that it is thus selective.

Lüppo-Cramer has tried to obviate this by the idea that the "weak" developers which are catalyzed by KI are those which usually give only "grain surface" development, not penetrating the grain. But actually there is no evidence that hydroquinone does not give complete development of the grain, and a spongy silver grain. Further, with such a weak, or low, potential developer as ferrous oxalate, which is much more inclined to grain surface development, the Lainer effect is very slight or even absent."[18] This was again tested on the "time of appearance," using a Chapman-Jones plate tester with a constant light source.

TABLE I.

Effect of KI on Time of Appearance of Image.

Seed Process Emulsion; Ferrous Oxalate Developer.

Expt.	Developer Concn.	Treatment.	Time in sec. Average of 2 expts.
1	N/10	H_2O	18
		N/10000 KI	11
		N/1000 KI	37
		N/100 KI	95
2	N/20	H_2O	45
		N/10000 KI	47
		N/1000 KI	75
		N/100 KI	157
3	N/10 Pure Bromide Emulsion	H_2O	23
		N/10000 KI	39
		N/1000 KI	49
		N/100 KI	110

Experiments (1) and (2) were made on Seed process emulsion, experiment (3) on pure bromide emulsion. It will be seen

[17] S. E. Sheppard and G. Meyer, *loc. cit.*

[18] Dr. Lüppo-Cramer has pointed out, since this was written (private communication) that von Hübl first obtained the Lainer effect with ferrous oxalate, and that he has also obtained it. It must be concluded then, from our negative results, that emulsion variations come in here (*cf.* S. E. Sheppard, *Phot. J.*, 46, 88 (1922)).

that, except in one instance, there is no acceleration but rather a retardation produced by pretreatment with potassium iodide. But with hydroquinone a very definite acceleration was produced:

TABLE II.

Effect of KI on Time of Appearance of Image.
Seed Process Emulsion; Hydroquinone Developer.

Expt.	Developer.	Treatment.	t in sec.
4	Hydroquinone 5.6 gms. Na_2SO_3 36 gms. Na_2CO_3 75 gms. H_2O 1000 c.c.	H_2O N/10000 KI N/1000 KI N/100 KI	29 14 20 35
5	Ditto + the iodide*	H_2O N/10000 KI N/1000 KI N/100	29 28 25 15

* The difference when iodide is added to the developer had already been noticed (Sheppard and Meyer, *loc. cit.*).

With p-amidophenol, no acceleration was observed.

TABLE III.

Effect of KI on Time of Appearance of Image.
Seed Process Emulsion; p-amidophenol Developer.

Expt.	Developer.	Treatment.	t in sec.
6	P.A.P.	H_2O N/10000 KI N/1000 KI N/100 KI	12 15 21 45

While ferrous oxalate is very insensitive to potassium iodide, it shows marked acceleration in the presence of sodium sulphide, polysulphides, and sodium thiosulphate (*cf.* Table IV).

Yet these substances (sulphides and thiosulphate) have no such action with hydroquinone or other organic developers; further, their catalytic action with ferrous oxalate varies considerably from one emulsion to another. Taking these facts into consideration, the explanation of development catalysis by mechanical

nucleus exposure appears inadequate. The effects are too specific, and can be accounted for on other grounds.

III. NUCLEUS EXPOSURE AND OXIDIZING TREATMENTS.

If the Lainer effect and related effects do not necessitate "nucleus exposure" any more than the previously described influence of silver iodide in physical development, are there any cases in which it is a useful hypothesis? It is evident that if "nucleus exposure" facilitates reduction, by "freeing" the silver

TABLE IV.

Effect of Na_2S; Polysulphides; and Na_2S_2O on Appearance of Image. Ferrous Oxalate Developer.

Expt.	Plate.	Developer. Concn.	Treatment.	t in sec.
8	Pure bromide	N/10	NaSH Bathed	
			H_2O	21
			N/100000	28
			N/10000	10
			N/1000	Fog
9	Seed process	N/10	NaSH Bathed	
			H_2O	17
			N/100000	30
			N/10000	61
			N/1000	Fog
10	Seed process	N/10	$Na_2S_2O_3$ Bathed	
			H_2O	13
			N/10000	12
			N/1000	3
			N/100	<3
11	Seed process	N/20	$Na_2S_2O_3$ In developer	
			H_2O	40
			N/100000	37
			N/10000	34
			N/1000	16

nuclei, equally it should facilitate destruction of such nuclei by oxidizing agents. Experiments on this have been carried out both on the latent image and on the sensitivity.

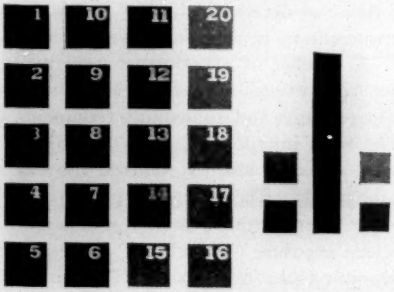
It should be noted that we must distinguish between at least three grades, or regions, of sensitivity and latent image, for any

given emulsion, according to the method of development. In terms of increasing exposure, we have broadly:

→ Exposure		
Sensitivity and latent image by chemical development	Sensitivity and latent image by physical development previous to fixation	Sensitivity and latent image by physical development after fixation

The experiments next to be described are of an orienting character, and only semi-quantitative. That is to say, instead of

FIG. 1.



The Chapman-Jones plate tester.

measurements of the characteristic curves, the extent of scale, or the "schwellen wert," of a conventional plate tester was used. This was a Chapman-Jones plate tester [19] (Fig. 1). Such testers have been invaluable in orienting, pioneer, and routine work, although not suitable for precision sensitometry.

Exposures were made to a 5-watt lamp, run off accumulators, and kept at a constant e.m.f. and amperage. The references to "degrees C. J." will be clear from the figure.

[19] Chapman-Jones, "Science and Practice of Photography," London, 1904, p. 546.

IV. FOGGING ACTION OF POTASSIUM IODIDE BATHS.

Apart from the "red sensitizing" effect of iodide,[20] treatment of silver bromide plates with dilute KI solution leads to chemical fog, shown both for chemical and physical development.[21] It is, however, much more marked in the case of physical development. According to the "nucleus exposure" hypothesis, the action is due to the disinterring of interior silver nuclei, large enough or active enough [22] to initiate reduction in a developer. It is somewhat difficult to reconcile with this the greater tendency to production of "fog" by iodide for physical than for chemical development, since generally a considerably lower "nucleation threshold" is sufficient in the latter case.[23]

If it be assumed that any silver iodide formed is less easily reduced on chemical development, why is this not operative for the same treatment in accelerating development with hydroquinone, etc.? A number of experiments were made, "spotting" plates of pure AgBr emulsion (no iodide) with dilute KI solutions. Further, both previous and subsequent treatments with chromic acid solutions were interpolated, with the object of destroying either original surface reduction centres, or such as might be exposed by the iodide. The results are given in Table V.

These experiments certainly do not give definite confirmation of the "nucleus exposure" hypothesis. In particular, the treatment with chromic acid *after* iodizing did not markedly reduce the fogging action of this, while treatment with chromic acid *prior* to iodizing did. This result is possibly due to the chromic acid treatment, in the second case, interfering with the iodizing by tanning the gelatin. In any case, the results seem more consistent with the adsorption hypothesis. The same results were obtained with a standard lantern emulsion. With this also the iodide fog on chemical development was much less than with physical

[20] S. E. Sheppard, "Action of Soluble Iodides, etc.," *Phot. J.*, **46**, 88 (1922).

[21] *Ibid.*

[22] Such ambiguity must be allowed in absence of precise knowledge.

[23] *Cf.* footnote (22). This corresponds to the greater light sensitivity of emulsions when chemical development is used.

TABLE V.

Fogging "Spot" Tests with KI on Pure AgBr Emulsion.

Expt. No.	Treatment.	Mode of Development.	Effect at			
			0	N/10000	N/1000	N/100
473	Spotted with KI solutions	Physical before fixation	None	Faint	Med.	Heavy
		Chemical	None	Faint	Med.	Med.
474	Spotted with KI. Then treated with .05 per cent. CrO_3 + .01 per cent. H_2SO_4 for five minutes. Rinsed and sulphated, washed.	Physical	None	Faint	Med.	Med.
475	Treated first with 5 per cent. CrO_3, washed, etc., dried, then spotted with KI	Physical	None	Faint	Med.	Med.
478	Same, chronic acid, etc., as in 475	Chemical*	Faint	Med.	Med.	Med.
480	Spotted with KI, then treated with 1 per cent. CrO_3 + .25 per cent. H_2SO_4, washed, etc.	Physical	Faint	Med.	Med.	Med.
481	Same as 480, but followed CrO_3 with sod. bisulphite	Physical	Faint	Faint	Med.	Med.
482	Treated first with 1 per cent. CrO_3, washed, etc., then spotted with KI	Physical	None	None	Very faint	
483	Same, but used intermediate bath of bisulphite then KI	Physical	None	None	Very faint	

* Showed reversal at centre of spot.

development, and the effect of a chromic acid treatment was greater when used before than when used after iodide spotting.

V. POTASSIUM IODIDE TREATMENT AND THE REGENERATION OF LATENT IMAGE.

The extensive and valuable investigations of Renwick [24] have shown that the silver bromide of an exposed emulsion may be practically entirely converted to silver iodide with only slight loss of "latent image." Renwick's results have been confirmed and

[24] Hurter Memorial Lecture, *J. Soc. Chem. Ind.*, 39, 156T (1920).

elaborated by Lüppo-Cramer.[25] We shall not deal here with this reaction, but merely note that even strong potassium iodide solutions, provided the oxidation potential is kept down, have no marked destructive effect on the latent image. The effect we have to deal with now is one observed by Lüppo-Cramer [26] and affords, when positive, the strongest evidence yet adduced in favor of his original "nucleus exposure" hypothesis. As such, he has recently [27] introduced it in rebuttal of Sheppard and Meyer's criticism of his explanation of the Lainer effect. The new effect consists in the regeneration of latent image by treatment of an exposed plate with potassium iodide after it has been treated with chromic acid. It will be seen that the experiment is of the same type as that just discussed for fog. Lüppo-Cramer states that latent images on lantern plates were freed from the *soluble latent image* [28] by treatment with a chromic-sulphuric acid mixture; after thorough washing out of the chromic acid, which could be accelerated by pickling with concentrated Na_2SO_4 or KNO_3 solution,[29] one of the two plates thus treated was bathed one-half minute in a one per cent. KI solution, and then developed in the same physical developer as the other. The iodided plate showed after three minutes the whole Chapman-Jones scale, while the control gave nothing after thirty minutes. "Similar results were obtained with synthetic photobromide and photochloride."

[25] "Kolloidchem. u. Photographie," 2nd Ed.

[26] *Ibid.*

[27] *Koll. Zeit.*, 30, 186 (1922).

[28] Lüppo-Cramer considers, by this, that the latent image consists of a superficial portion, immediately active in ordinary developers, but easily removed by oxidizing agents, and an interior, more protected part. This latter can only function in catalyzing development when "exposed," or laid bare, and is similarly secured from destruction by oxidation, until "exposed." It forms the chief portion of the "latent image developable after fixation"—corresponding to Sterry's "organic latent image" (*Phot. J.*, 22, 264 (1898)). This view, which is consistent with many, though not all, of the reactions of the latent image, is not always maintained in this definite form by Lüppo-Cramer. Thus while at one time he refers to the solution of the superficial latent image by chromic acid, at another (*vide infra*, p. 670) he supports Sterry's view that the effect of chromic acid is only to delay development (chemical) not to destroy the latent image.

[29] *Cf. Phot. Ind.*, 1912, p. 572. Similar to the use of brine in the leather industry to pickle hides after souring.

In Table VI are given orienting results on the effect of chromic acid at different concentrations on (*a*) the latent image, (*b*) the sensitivity. These terms are used here formally, to signify that in case (*a*) the chromic acid, etc., treatment was used *after* exposure, before development, and in (*b*) *before* exposure. In saying provisionally that the effect in case (*a*) exhibits the destruction of "latent image," this shall not be interpreted as meaning complete

TABLE VI.

Action of Chromic Acid on Latent Image (a) and Sensitivity (b).

Treatment (5 minutes).	After-treatment.		Degrees Chapman-Jones.											
			Seed Graflex.		Seed Lantern.		Seed Process.		News Bromide		Contrast Velox.		Lippmann (washed).	
		S.*	173,000		5400		5400		1320		6		1	
Blank.	Blank.		25		25		25		25		25		23	
			a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
CrO_3 5% / H_2SO_4 1%	$NaHSO_3$ 5%		0	0										
CrO_3 2% / H_2SO_4 5%	$NaHSO_3$ 5%		0	19	0	14	0	15	0	15	18	25	0	25
CrO_3 1% / H_2SO_4 .25%	$NaHSO_3$ 5%		14	20										
CrO_3 .5% / H_2SO_4 .125%	$NaHSO_3$ 5%		15	22	0	17	0	18	15	17	20	25	0	25
CrO_3 .25% / H_2SO_4 .06%	$NaHSO_3$ 5%		16	23	0	20	0	18	19	19	21	25	0	25
Development.....			P.A.P. 4 mins.		P.A.P. 4 mins.		P.A.P. 4 mins.		P.A.P. 4 mins.		Nepera 1:4 4 mins.		P.A.P. 15 mins.	

* S refers to relative sensitivity, in terms of Lippmann emulsion as 1.

destruction, nor even as excluding paralysis of developability. Effectively, so much latent image is put out of action for a given type of development. Similarly, in case (*b*) any apparent or effective desensitizing may be due either to actual reduction of sensitivity prior to exposure, or to something remaining after the treatment, which destroys, or inhibits, the nascent "latent image." [30] This latter possibility is largely discounted in the

[30] *Cf.* Sheppard and Mees, "Theory of the Photographic Process," p. 197.

present case, because the after-treatment with bisulphite destroys any chromic acid, converting it to chromium sulphate [31] which, although it tans the gelatin, does not affect either sensitivity or appreciably inhibit development. This was determined by separate and special tests, some of which will be described now.

VI. THE RETENTION OF CHROMIC ACID AND CHROMIUM SALTS BY GELATINO-SILVER BROMIDE EMULSION.

1. *Adsorption of CrO_3 to Precipitated AgBr.*

It has been previously suggested by one of the authors and C. E. K. Mees [32] that chromic acid is appreciably adsorbed to silver bromide. This possibility has now been tested, using pure silver bromide precipitated in the dark in absence of gelatin. The AgBr was prepared by mixing equal volumes of:

(*A*) Solution of KBr 20.6 gms. in 250 c.c.
(*B*) Solution of $AgNO_3$ 29.4 gms. in 250 c.c.

Using 25 c.c. each of *A* and *B*, 5.0 gms. AgBr are formed. This was precipitated in red light, washed by decantation, and treated for twenty-four hours with chromic acid solution. The chromic acid in the solution was determined by the method of Fresenius and Cohn [33] with ferrous sulphate and permanganate. The results are given in Table VII.

TABLE VII.

The Adsorption of CrO_3 by AgBr.

Concentration of CrO_3.	Gms. CrO_3 absorbed per 5 gms. AgBr.
.50 per cent.	.000
1.00 per cent.	−.001
2.00 per cent.	−.00036
3.00 per cent.	+.00036
4.00 per cent.	+.0003
5.00 per cent.	+.0005

The adsorption, measured by the effective change in concentration, is less than the error of the method; it appears in any

[31] Actually a complex chromium sulphate.
[32] "Theory of Photographic Process," *loc. cit.*
[33] Fresenius and Cohn, vol. i, p. 424, New York, 1912.

case to be less than 0.0001 g. per 1 gm. AgBr. Control experiments on washing out chromic acid from the precipitate showed this to be washed out quantitatively according to the usual law, no appreciable quantity of chromic acid being left. Hence, it is concluded *that there is no appreciable adsorption of chromic acid to pure AgBr in absence of gelatin.*

2. *Retention of CrO_3 by Gelatin.*

The problem of the complete removal, or at least neutralization, of desensitizing and image destroying substances, prior to the operations of exposure and development, respectively, has seldom received sufficient attention. Yet where "topochemical" inferences are drawn from the results of a series of reactions carried out on the plate, for them to be convincing, proof is necessary that the earlier reagents have been removed. It is well known that the complete removal of certain substances from gelatin is a very difficult matter. As regards chromic acid, recent investigations [34] suggest that while this will combine with gelatin at H-ion concentrations less than $p_H = 4.7$, above this it should be uncombined and readily washed out.

We have found that careful neutralization of the chromic acid in the emulsion by treatment with solutions of Na_2CO_3 and $NaHCO_3$ is much more effective than either repeated washing alone or the "pickling" process of Lüppo-Cramer.

As illustrating the retention of chromic acid after repeated washing, 150 sq. cms. of Seed graflex plate were soaked two hours in a solution of .25 per cent. CrO_3, .06 per cent. H_2SO_4, and then washed in ten changes of distilled water, ten minutes each. The emulsion was then stripped, ignited, the reduced chromium oxidized to CrO_4'' with chlorine, and determined. Found .0235 gm. CrO_3 per 150 sq. cms.

When 5 per cent. $NaHCO_3$ was used for ten minutes, and only four washes in distilled water, only .002 gm. CrO_3 were found. If instead of Na_2CO_3 or $NaHCO_3$, sulphites, as Na_2SO_3 or $NaHSO_3$, are employed, chromic acid is reduced to the chromic condition (in part probably as complex anion). This has no

[34] *Cf.* J. Loeb, "Proteins," New York, 1922.

appreciable oxidation-potential as regards either the "sensitivity" or the "latent image."[35]

But in order to be sure of this, it appeared desirable to be able to remove the chromium, which is now tenaciously retained by the gelatin, forming a chrome tanning. To effect this, advantage was taken of the action of polyhydroxy organic acids in dissolving chrome oxide and effecting detanning.[36] In the case of chrome-hardened gelatin, the solutions must not be too concentrated nor the temperature too high, or the gelatin becomes peptized. The following results were obtained with the same emulsion hardened for two hours in 1.25 per cent. chrome alum solution.

TABLE VIII.

Removal of CrO_3 from Plates.

No.	After-treatment.	M. P. °C.	Gms. Cr per 100 sq. cms.	Gms. Cr per gram dry emulsion.
0	(Blank)	37° – 38°		
1	Rinsed only	>100°	.0055	.0143
2	3 washes 15 mins. in 3 per cent. citric acid	60° C.	.0011	.00287
3	3 washes 1 hr. in 3 per cent. citric	55° C.	.0008	.00205
4	3 washes 1 hr. then 15 hrs. in 3 per cent. citric	45° C.	.0003	.00082
5	3 washes 1 hr. then 15 hrs. in 5 per cent. citric	38° C.	.00008	.00020

It is concluded that a preliminary treatment with 3 per cent. citric acid, followed by 15 to 18 hours in 5 per cent. acid, kept at or below 60° F., removes all but traces of Cr. At the same time, the process is tedious, and generally unnecessary. It served to show that Cr retained by the gelatin had no pronounced inhibiting effect either upon exposure (sensitivity) or upon development (latent image).

3. *Possible Effects of CrO_3 on the AgBr Emulsion and the Treatment Used Practically for Removal of CrO_3.*

The question of removal or destruction is of critical importance. When a plate is treated (*A*) before exposure, (*B*) after

[35] Regarding "sensitivity" as partly determined, at least, by a precursor of the latent image other than silver halide.

[36] H. R. Procter and J. A. Wilson, *J. Soc. Chem. Ind.*, 35, 156 (1916).

exposure, before development, the effects observed might be due to the following conditions:

	A Before Exposure.	*B* After Exposure, Before Development.
(*a*)	The oxidizer may destroy sensitizing nuclei. These may be colloid silver, or traces of substances in gelatin.	The oxidizer may destroy the latent image.
(*b*)[37]	The oxidizer, remaining in the emulsion, may destroy the nascent latent image.	The oxidizer may inhibit the development, *e.g.*, *poison* the development centres.

(*c*) The oxidizer, remaining in the emulsion during and after exposure, may interact with the developer and reduce its concentration.

Of these, case (*c*) was applied by Sheppard and Mees to explain part of Sterry's results[38] with chromic acid. It was not suggested that all the phenomena were accounted for, since either an apparent destruction, or at least inhibition, of the latent image was observed, depending considerably upon the time of action and the concentration of chromic acid. This part of the action was unaffected by treatment of the chromated plates with neutral sodium sulphite previous to development.[39]

Neutral sodium sulphite (Na_2SO_3) can have an independent action on the silver halide grain. This consists in partial solution and formation of a soluble complex silver salt, perhaps more readily reducible. It is in any case desirable to reduce this tendency, as well as the tendency to reduction, and for these reasons the bisulphite is preferable. It also produces a tanning complex with the chromic acid, which can be removed with citric acid if necessary.

In most cases, for relatively short treatment with not too concentrated CrO_3—up to 2 per cent.—we find that a bath of 5 per cent. $NaHCO_3$, followed by good washing, is sufficient to remove the CrO_3. For "one-grain layers," subsequently noted, this treat-

[37] This theory of desensitizing (Sheppard and Mees, "Theory of Photographic Process," p. 261) has been adopted by Lüppo-Cramer for his safranin desensitizing process.

[38] *Phot. J.*, **54**, 50 (1904).

[39] Sheppard and Mees, *loc. cit.* *Cf.* also Lüppo-Cramer, *Phot. Korr.*, 1909, p. 496. This author refers here to the use of sulphite for eliminating chromic acid, but misses the point since he overlooks the fact that Sheppard and Mees differentiated between the transient and the permanent effects of chromic acid.

ment is entirely adequate, but for ordinary emulsions the removal of CrO_3 must be tested.

VII. DESTRUCTION OF SENSITIVITY, AND REGENERATION.

Returning now to consideration of the results in Table VI, it will be seen that, generally, as the speed and the grain-size decrease, the "sensitivity" appears to be relatively less affected than the "latent image." The explanation of this does not appear to be in an actually greater resistance of the "sensitivity" in the finer grains. It is due to a sensitizing action of the bisulphite, which can be shown to have an actual independent sensitizing action on emulsions such as Lippmann, and even Seed process. Consequently, the Velox and the Lippmann emulsions do not show any desensitizing effect with this treatment, although in the latter case the "latent image" was wholly obliterated.

The bisulphite cannot regenerate "latent image" (which is differentiated or has gradation) and does not produce the analogue at this stage (after exposure), *viz.*, general chemical fog, to any great extent. Owing to this resensitizing effect, the results recorded here are of more importance for the "latent image," for which a considerable measure of destruction appears to be effected.

It has been asserted by Sterry [40] and by Vidal [41] that the apparent destruction of the latent image by chromic acid is mainly a matter of retardation of development. Lüppo-Cramer's differentiation of the "latent image" into superficial, more soluble, and occluded, strongly adsorbed, less soluble portions has helped to clarify the issue here, particularly in regard to the residual "latent image" physically developable after fixation.

But Lüppo-Cramer has also stated [42] that "furthermore the image appears almost unchanged, if ordinary development is only very greatly prolonged." This did not agree with results previously obtained by one of us (S. E. Sheppard) and was retested. It appeared more probable with fine-grained plates, which would be relatively more susceptible of a certain amount of secondary development, *i.e.*, combined fixation, by sodium sulphite, and physical development.

[40] *Phot. J., loc. cit.*
[41] *Photo. Archiv.*, 1895, p. 344.
[42] *Phot. Korr.*, 1909, p. 495-496.

Seed lantern plates were treated with 2 per cent. CrO_3, which was found to apparently destroy the latent image for ordinary development. An after-bath of 5 per cent. $NaHSO_3$ was used to destroy the residual CrO_3. Development was effected with a solution of

7 grams p-aminophenol hydrochloride
50 grams Na_2CO_3
50 grams Na_2SO_3
1000 c.c. with water

This contains sufficient sulphite (5 per cent.) to exercise the "nucleus exposing" action asserted by Lüppo-Cramer,[43] or the possibly equivalent "secondary development" referred to above.

It was found that neither prolongation of the development for many hours, nor frequent renewal produced any trace of image. Yet when the same CrO_3 solution was used prior to exposure, and followed by bisulphite, about 17 to 18° C. J. were immediately and normally developed, as compared with 25° with no CrO_3 treatment. Tests on other plates gave the same result, so that we are unable to confirm the idea of mere retardation of development. It appears that chromic acid, at sufficient concentration, destroys most of the latent image active in normal chemical development.

Returning to Table VI, it will be noted that the latent image on N-bromide and on Velox shows considerably greater resistance than on the plates (Process, etc.) of coarser grain. This is due to difference of chemical composition. The Velox emulsion is practically entirely silver chloride, while the N-bromide contained considerable chloride as well as bromide. This result then is quite in agreement with Lüppo-Cramer's general conclusion that in the series

$$AgCl \longrightarrow AgBr \longrightarrow AgI$$
$$Ag_x(AgCl)_y \longrightarrow Ag_x(AgBr)_y \longrightarrow Ag_x(AgI)_y$$

the photohalide stability *decreases* from the chloride to the iodide, or, in other words, the adsorption of colloid silver is strongest in the chloride.

[43] *Phot. Korr.*, 1912, p. 313. "Further experiments showed that the simple sulphite solution alone had a nearly equal effect [to that of 10 per cent. potassium ferrocyanide plus 5 per cent. sulphite] on the latent image treated with chromic acid."

TABLE IX.

Action of CrO_3 and KI on Latent Image.
Graflex Plate; Exposed 20 sec. to Standard Light.
Developed 4 min.

Expt.	Treatment.				Result in Degrees C. J.	
	1	2	3	4	Phys. Develop.	Chem. Develop.
487	Nil-Dry Plate				16	
527	Nil-Dry Plate				14	
528	Nil-Dry Plate				16	
491	Nil-Dry Plate					25
529	Washed, H_2O				19	
530	Washed, H_2O				20	
488	1% KI	Washed, H_2O			22	
492	5% Na_2SO_3 1.5 min.					23
489	1% KI	0.05% CrO_3	5% $NaNO_2$	Washed	15	
493	1.5 min. Washed	0.01% H_2SO_4 5 min.	5 min.			24
490	1% KI	0.05% CrO_3	5% Na_2SO_3	Washed	21	
517	5% Na_2SO_3	0.01% H_2SO_4	5 min.		19	
494	1.5 min.	5 min.				22
519	Washed					22
507	1% KI 5% Na_2SO_3 1.5 min. Washed	0.05% CrO_3 0.02% H_2SO_4 5 min.	Washed		22	
508	0.05% CrO_3	12% Na_2SO_4			15	
518	0.01% H_2SO_4				12	
525	5 min.		Washed		13	
526					19	
505						25
520						25
503	0.05% CrO_3	12% Na_2SO_4	1% KI	Washed		23
506	0.01% H_2SO_4 5 min.	Pickled and washed	5% Na_2SO_3 1.5 min.		24	
509	1% KI 5% Na_2SO_3 1.5 min.	0.2% CrO_3 0.04% H_2SO_4 10 min.	Washed			15
510	0.2% CrO_3 0.04% H_2SO_4 10 min.	1% KI 5% Na_2SO_3 1.5 min.	Washed			15

TABLE IX (*cont.*).

Action of CrO_3 and KI on Latent Image.
Graflex Plate; Exposed 20 sec. to Standard Light.
Developed 4 min.

Expt.	Treatment.				Result in Degrees C. J.	
	1	2	3	4	Phys. Develop.	Chem. Develop.
511	Same	1% KI No sulphite	Washed			15
512	Same	No KI	Washed			19
513	1% KI 1.5 min.	0.2% CrO_3 0.05% H_2SO_4 10 min.	5% Na_2SO_3 10 min.	Washed	13	
514	0.2% CrO_3 0.05% H_2SO_4 10 min.	12% Na_2SO_4	1% KI	Washed	20	
515	1% KI 1.5 min.	0.2% CrO_3 0.05% H_2SO_4 10 min.	Washed		0	
516	0.2% CrO_3 0.05% H_2SO_4 10 min.	Washed			0	
521	0.2% CrO_3 0.04% H_2SO_4 10 min.	12% Na_2SO_4 Washed	1% KI 5% Na_2SO_3 Wash	Repeat 1, 2, and 3, then wash	14 wet	
522	0.1% KI 5% Na_2SO_3 1.5 min.	0.2% CrO_3 0.04% H_2SO_4 washed	12% Na_2SO_4	Repeat KI then Wash	15 wet	
		Developed 8 min. instead of 4 min.				
520	0.2% CrO_3 10 min.	12% Na_2SO_4 10 min.	Washed			19
523			Washed			19
524			0.5% KI 5% Na_2SO_3 1.5 min.	Washed		20

(*To be concluded.*)

The Auroral Spectrum and the Upper Strata of the Atmosphere. L. VEGARD. (*Phil. Mag.*, July, 1923.)—In Professor Vegard's expedition to Bossekop in Finmarken during the winter of 1912–13 he photographed some of the blue lines in the

auroral spectrum. These were shown to belong to the negative band spectrum of nitrogen. In the winter of 1921 he continued his investigations at Christiania, where he is professor of physics, and measured the wave-length of the characteristic green line in the spectrum of the aurora. This equalled 5578.0 international units. Its origin, however, remained unknown. Last winter, 1922–23, three spectrographs at the Geophysical Institute, Tromso, were used by him in further examination of the aurora. With an exposure of 15–20 hours the quartz spectrograph furnished a photograph of 21 lines. Thirty-five lines in all were measured, of which 29 belong to nitrogen and two are most likely bands of the same gas. There remain four lines of unidentified origin, of which one is the green line. "I think," he says, "there is little doubt that these lines also are due to nitrogen. This only means that the auroral spectrum is formed under conditions which are very difficult to reproduce in the laboratory." He emphasizes that "no indication of either hydrogen or helium lines has been observed." He has studied the light produced when cathode rays bombard a mixture of nitrogen and hydrogen on the one hand, and of nitrogen and helium on the other, and draws the conclusion, "The absence of H and He lines in the auroral spectrum, therefore, shows that in that region where the auroral light is emitted, the pressure of H and He must be small compared with that of N in the same region." This deduction is recognized to be contradictory to the results drawn from the assumptions of Wegener and also to the existence of a temperature of 300° absolute in the upper parts of the atmosphere derived by Lindemann and Dobson from a study of meteors. According to both of these other methods there should be a predominance of helium and hydrogen over nitrogen at a height of about 140 km. above the surface of the earth. This is in addition negatived by the consideration that there should be a change in color of the auroral rays as they pass from heights of 300 km. down to 110 km. above the earth, were there such a notable change in the composition of the atmosphere along their path.

"I have found by spectral observations that the green line is seen to the very top of the auroral ray streamers, and the gas which emits this line must be a prominent component of the atmosphere up to its extreme upper limits. Hence we conclude that the hydrogen and helium layer, which has earlier been supposed to dominate at the top of our atmosphere, does not exist." He rejects the possibility of the origin of the line being due to a hypothetical element geocoronium. "The introduction of geocoronium is merely an easy way of getting out of the difficulty."

As a solution of some of the problems of the aurora the author suggests that the radiation of very short wave-length from the sun may drive negatively charged electrons from the nitrogen of the higher regions in the atmosphere. Thus there is left surrounding the earth a shell of positively charged nitrogen and by this the famous green line may be emitted. G. F. S.

CORRESPONDENCE.

University of London, University College.
Gower Street, London, W. C. 1.
20th September, 1923.

Dear Sir,

I venture to send you the enclosed note for publication in your JOURNAL if it meets with your approval. It contains a short answer to R. W. G. Wyckoff, who in previous issues of your JOURNAL has criticized our work on the X-ray analysis of crystals.

Yours faithfully,

(Signed) W. H. BRAGG.

The Editor, of the
JOURNAL OF THE FRANKLIN INSTITUTE,
Philadelphia.

R. W. G. Wyckoff, discussing recently the relation between the X-ray analysis of crystalline structure and the conclusions of mathematical crystallography, has made statements (JOURNAL OF THE FRANKLIN INSTITUTE, Feb., March and April, 1923) which demand a reply. He condemns *in toto* all attempts at analysis which, as he puts it, have paid insufficient attention to the theory of space groups.

The theory of space groups is the final effort of geometrical crystallography: "The geometrical theory is now complete" (Hilton, "Mathematical Crystallography," p. 256). Having proved that there are 32 classes of crystal in regard to symmetry, as defined by the possession of different combinations of centre axes and planes of symmetry, it proceeds to show that in each class the possession of a particular combination is compatible with various relative positions of the axes and planes in space. The existence of a plane of symmetry may be due to the fact that the atoms and molecules of the crystal become self-coincident after direct reflection across the plane; or they may become so only after a shift in some direction or another; the same alternative is found in the case of an axis. In the cubic system, the axes of trigonal symmetry, which are necessarily present, may or may not intersect. Within each class, therefore, are variations of the actual movements which can bring the crystal to self-coincidence. Each such set of movements constitutes a "space group of movements." In all, there are 230 such sets, distributed among the 32 classes.

Now we may state this classification in another way. A crystal may be looked on as an aggregation of sets of atoms, which we may

call molecules since they are generally identical with chemical molecules. Given a certain number of molecules with which to form the unit pattern, it is possible to arrange them so that the unit and the crystal have certain degrees of symmetry, in other words, so that the crystal belongs to some one of the 32 classes. But, given the number and the class, there are in general several ways of arranging the molecules so as to obtain the symmetries of the class. Each of these ways corresponds to one of the 230 space groups, and each of the 230 can, therefore, be described in two ways. Given the necessary data as to the positions of the molecules, *i.e.*, as to the absence or presence of shifts, the various movements can readily be deduced, and *vice versa*.

If a crystal is examined by the older methods which depend on observations of form, its class can nearly always be determined, but not its space group. On the other hand, the X-ray methods can do all that the older methods could do except that they cannot detect the existence of a centre of symmetry and can also determine, in a great number of cases, those data regarding the relative positions of the molecules by which its space group is defined. This being done, the system may be denoted by the name or symbol which mathematical crystallography has given it. But no help towards the determination of structure is to be obtained in this way, because nothing has been, or can be, discovered about any space group except the possibility of its existence. The point up to which the study of symmetry can be of assistance has already been passed. Up to that point, the conclusions of mathematical crystallography can be most helpful in saving time and labor, though they can only prove the possibility of what the X-rays actually find. Beyond that point new ground is entered.

It is unreasonable, therefore, to reject results because they have been obtained without the use of the terms of the theory of space groups, since the terms which are more naturally used in the X-ray analysis are equally effective in expressing the laws of symmetry.

Let us take an instance. Suppose we are examining by the X-rays a crystal which has been shown by the older methods to belong to Class 7, the rhombic hemimorphic class: Such a crystal is resorcinol. The results of X-ray analysis show that the crystal unit cell is orthorhombic and contains four molecules, and they determine the dimensions of the cell. We now take into account the known polarity of the crystal and then conclude that the molecule has no symmetry: Since the crystal would belong to a class of higher symmetry if its four molecules had symmetry of their own. We might even be justified in assuming the asymmetry of the molecule at once, from previous knowledge of the characteristics of such a molecule.

The results show further that the spacings of the $(0\ m\ n)$ and $(1\ 0\ m)$ planes are halved unless $(m+n)$ and $(1+m)$ are even. This shows that the arrangement of the molecule is as follows:

Let one of the four molecules be placed at each of the eight

corners of the cell. Let a second, which is the reflection of the first in a plane parallel to the yz face of the cell, be placed so that its projection on that face is at the centre of the face. Correspondingly, for the third molecule reflected in the xz face. The position of the fourth molecule is determined by the positions of the others.

The space group of the arrangement thus arrived at is known to geometrical crystallography: The possibility of its existence has been foretold, and the symbol C_{2v}^{10} has been assigned to it.

If the asymmetry of the molecule could neither have been proved nor assumed, there would have been an alternative to the above classification. The crystal might have been holohedral and its space group Q_h^{12}.

Geometrical crystallography could not have carried the argument so far; nor can it be of any use whatever in carrying it farther. But the point to which we wish to draw particular attention is that it is not necessary to employ the terminology of the space group theory at any stage; and in the early experiments its use would have been very confusing.

Repulsion Effect between the Poles of an Electric Arc. H. M. BARLOW. (*Phil. Mag.*, July, 1923.)—"I suggest that the evidence is in favor of the view that at least a measurable part of the repulsion effect in an arc is due to the 'pinch' phenomenon operating in the gaseous conducting column between the poles." "A conductor may be imagined to consist of a large number of filaments parallel to the axis, each carrying part of the total current. All the filaments except the one on the axis will experience a force tending to urge them toward the centre. If, therefore, the conducting column is mobile, it will contract so as to diminish its cross-section and, in consequence, increase in length. . . . Although a gas will not normally resist change of pressure, we have to remember that in the case of an arc the radial striction forces are exerted more or less uniformly along its whole length, so that the ionized vapor is kept within a confined space. The system is analogous to a rubber tube containing gas under pressure and having rigid plugs in its ends." The poles of the arc are these plugs and they are pushed apart by the filaments of current crowding in toward the axis. Other forces must be present in addition since a calculation shows that the "pinch" effect is competent to account for only 30 per cent. of the observed repulsion.

G. F. S.

An Apparatus to Demonstrate the Effect of Dust Particles, Ions and Electrons in the Production of Clouds. C. LAKEMAN and R. SISSINGH. (*Physik. Z.*, June 1, 1923.)—By this piece of apparatus a whole audience can see the path of an alpha particle that has ploughed its destructive way through a mass of air.

G. F. S.

Loss of Sunlight at Paris and in its Suburbs. L. BESSON. (*Comptes Rendus*, January 15, 1923.)—By means of Bellani's integrating actinometer a study has been made of the quantity of sunlight received directly and indirectly in summer at ten stations in or near to Paris. The results have been plotted in such a way as to bring out their relation to the direction of the wind at the time of observation. For example, at Ville Evrard, situated to the east of the capital, the light is represented in quantity by .83 when the wind is from ENE to S, while it is as .62 with a wind from the WNW. In the latter case the wind brought to the observing station the smoke of Paris, and a loss of 25 per cent. in the light was the consequence. This is due to two causes, loss of atmospheric transparency and increase of cloudiness. The importance of the first of these is proved by observations extending over a period of nine years made at Montsouris at the middle of the day in summer under a clear sky. In regard to the second it has been found at Parc Saint-Maur, 8 km. from Paris, that a wind from the direction of the city sensibly reduces the duration of sunshine by reason of increased cloudiness. The radius of the effect is at least 10 km.

G. F. S.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

DYNAMOMETER TESTS OF AUTOMOBILE TIRES.[1]

By W. L. Holt and P. L. Wormeley.

[ABSTRACT.]

POWER-LOSS tests have been made on a large number of tires of different makes and sizes. From a study of the results, the following conclusions can be drawn. These are based on: No tractive effort, a speed of twenty-five miles per hour, and the normal axle loads and air pressures.

(*a*) The average loss in 30 × 3½ fabric tires is 0.71 horsepower; in cord tires, 0.48 horsepower.

(*b*) The average loss in 4-inch fabric tires is 0.94 horsepower; in cord tires, 0.67 horsepower.

(*c*) As an average, the loss in cord tires is approximately 70 per cent. of that in fabric tires.

(*d*) Extreme cases between the highest fabrics and the lowest cords show the cord with only 40 per cent. of the loss found in the fabric.

(*e*) Considering only the cord tires, the lowest loss for each size of tire is about 60 per cent. of that of the highest.

From the study of the causes for these wide differences, it is found that they are largely due to variations in carcass construction. The tread has a small effect and the tube (if of standard construction) very little, if any, effect on the power loss.

A large variation is found in the size of different makes of tires of the same rated size. The oversize or undersize feature has very little effect on the power loss, but has quite a large effect on the load-carrying capacity.

The amount which a tire is deflected, due to the axle load, is not a measure of the power loss. For the same deflection, overloading produces a more severe action on a tire than under inflation.

The power required to supply that absorbed by the tires and dissipated as heat must come from the fuel used, and, accordingly,

* Communicated by the Director.

[1] Technologic Paper No. 240, price ten cents.

a change in the kind of tires or the conditions under which tires are run will manifest itself in an increase or decrease in fuel economy. It is not out of the way to attribute a difference in fuel consumption of as much as 10 to 20 per cent. to changes in tires or tire conditions.

Probably the most important feature of dynamometer tests is that they furnish a means for accurately measuring the internal friction in tires. By means of progressive tests it is possible to closely trace just what takes place inside a tire and actually measure the effect of details of design and thus aid in coördinating more closely the different parts.

THE VISIBILITY OF RADIANT ENERGY.[1]

IN coöperation with the Nela Research Laboratories a new determination of the visibility of radiant energy has been made by the step-by-step method, an equality-of-brightness method with little or no hue difference in the two parts of the photometric field. Between 490 and 680 $m\mu$, inclusive, measurements were made upon fifty-two observers, some of them common to previous investigations; for thirty-eight of these observers measurements were continued to include 430 and 740 $m\mu$.

Energy values were based upon radiometric and spectrophotometric measurements made at the bureau, checked by an independent color temperature measurement at the Nela Research Laboratories. Luminosity values were obtained with a Brace spectrophotometer. The step was made by moving the collimator slit. The ratios of luminosities were measured with a Brodhun variable sector. The photometric field was the divided circle type subtending an angle of 3°. Brightnesses were safely above the Purkinje region, except, perhaps, at the end regions of the spectrum.

The method and apparatus are described in detail in the paper, and the results compared with those of other investigations. The conclusions reached may be summarized as follows:

(1) The final average values obtained fall within the values obtained in other investigations, except in parts of the outer regions of the spectrum.

(2) Comparisons between individuals common to other in-

[1] Scientific Papers, No. 475, price fifteen cents.

vestigations show on the average the same sort of agreement or disagreement as do the final average curves. There is evidence that the visibility of some individuals varies considerably from time to time.

(3) There is no certain difference between the average values of visibility obtained by the flicker and equality-of-brightness methods, provided the former is used under the experimental conditions recommended by Ives and the latter does not depart too widely from these conditions.

(4) This does not conflict with the conclusion of Hyde, Forsythe, and Cady and others that there is a difference between the visibility curves obtained by the two methods when the usual large Lummer-Brodhun field is used for the equality-of-brightness measurements.

(5) A revision of the I.E.S. mean curve is proposed which results in better agreement with the average experimental visibility data and still gives the same wave-length centre of gravity for light of a color temperature of 2077° K., as is given by Ives' physical photometer solution.

(6) The step-by-step method of measuring visibility is a reliable method with a precision comparable with that of the flicker method and much superior to the simple equality-of-brightness method involving large hue differences.

(7) Further statistical investigations would not seem to be as important as investigations into the effect of experimental conditions such as field size and brightness upon the visibility obtained by the two common methods of photometry. The investigations along these lines conducted by Ives should be supplemented and his conclusions verified, if correct, but with the step-by-step equality-of-brightness method rather than the one involving large hue differences, and with many more observers.

TESTS OF CAUSTIC MAGNESIA MADE FROM MAGNESITE FROM SEVERAL SOURCES.[1]

By P. H. Bates, Roy N. Young and Paul Rapp.

[ABSTRACT.]

THE properties of oxy-chloride cement have been studied, particularly in relation to the source (or properties) of the magnesite ores, conditions during the calcining process, and various

[1] Technologic Paper No. 239, price ten cents.

oxy-chloride cement mixtures. Ore from Greece, from two different sources in California, and from the State of Washington were used, as these were representative of the chief sources of supply for this country. They include two different types of ore, the first three being amorphous, and the last crystalline. Each ore was crushed and separated into three lots, differing only in size of particles. Size 1 contained the particles which passed a 1-inch screen, but was retained on a ½-inch screen; size 2 passed a ½-inch, but was retained on a No. 4 sieve; and size 3 passed a No. 4, but was retained on a No. 8 sieve. Each lot was then calcined in a 3 by 30-foot rotary kiln under fixed conditions throughout the operation. The temperature range, including all burns, was from 700 to 1100° C.

After grinding the caustic magnesia (the product from the kiln), the fineness, specific gravity, weight per cubic foot (loose and packed), loss on ignition, carbon dioxide content, and index of refraction were determined. There was difficulty in determining the fineness, particularly in the use of the No. 200 sieve, on account of the finest particles of the very active magnesias adhering to the screen or agglomerating into larger particles during the operation. There were wide differences between loose and packed weights per cubic foot, which brings out the importance of weighing caustic magnesia when making up mixtures, rather than measuring by volume as some do. Although a minimum and maximum carbon dioxide content has often been used in specifications for caustic magnesia, no relation was found between this constituent and the behavior of the oxy-chloride product. The index of refraction gives promise of being valuable in determining degree and uniformity of burning, but will not indicate changes in the material, occurring during storage, that have a marked effect on the properties of the cement. It was necessary to "age" some of the very active magnesias to make them usable.

Caustic magnesia from each lot was used in mixes prepared according to three flooring formulas, two stucco formulas, and one laboratory test formula. Only one concentration (22° Bé.) magnesium chloride solution was used for mixing with the dry materials, as this concentration is conceded to be the best for general use. Service tests were made in conjunction with the laboratory tests, and, therefore, the consistency of the wet mixture (excepting the laboratory test mix) was such as is generally used in

practice, and was kept the same in all cases, as nearly as possible. The service tests consisted of the laying of flooring panels; erection of stucco panels, all exposed to actual service conditions, and subsequent observations, including measurements of linear changes.

Three types of specimens were used in making strength tests: The briquette (of the shape used in the standard strength test for Portland cement mortar), for tensile strength; a ½ by 2 by 13-inch bar, for transverse strength; and a 2 by 4-inch cylinder, for compressive strength. In order to get an indication of the effect of intermittent wetting and drying of the set stucco during its early life, such as the material generally receives from exposure to the weather, specimens were tested in the following manner: After storing twenty-one days in the laboratory air they were placed in water for one day, followed by one day in air under certain temperature and humidity conditions. This cycle of water and air storage was repeated twice, and after an additional day in air (making twenty-eight days in all), the strength tests were made. Also, linear changes, resulting from this treatment, were determined. The laboratory specimens for expansion tests were ½ by 2 by 13-inch bars. The measurements were made by means of a 10-inch Berry gauge.

The results show that the various ores used require different conditions of calcination in order to produce caustic magnesias of approximately the same quality. Very light burning produces a magnesia which is too active for use in the customary oxychloride cement mixtures without "ageing" or the use of a retarder. An increase in the degree of calcination increases the time of set of the magnesia. Also, the degree of calcination affects, to a great extent, the strength, water resistance, and volume change of the set cement mixture. However, there are other factors which influence these properties nearly as much, if not more (within reasonable limits), than the burning. By the use of different types of aggregates with a magnesia, products, very different in behavior under test, may be obtained. Also, by changing the proportion of given aggregates, the products may be made to differ widely. Therefore, a magnesia considered good in quality may be made to give very unsatisfactory results, and one considered very poor often may be made to give excellent results.

STRESSES IN A FEW WELDED AND RIVETED TANKS TESTED UNDER HYDROSTATIC PRESSURE.[4]

By A. H. Stang and T. W. Greene.

[ABSTRACT.]

FOR the purpose of ascertaining the relative merits of riveted, as compared with electric-welded tanks, four steel tanks, four feet in diameter and ten feet long, made of $^5/_{16}$-inch mild steel plates, were tested under hydrostatic pressure. The tanks were designed for a stress of 16,000 lbs./in.^{2} at a working pressure of 200 lbs./in.^{2} Two of the tanks were butt-welded, one was lap-welded, and the fourth was of ordinary lap-riveted construction. The ends of the tanks were spherical, having a radius of four feet.

Strain gauge measurements were made at various portions of the tanks and at pressure increments of 50 lbs./in.^{2} until failure. The results of the hydrostatic tests proved rather unsatisfactory as a comparison of the relative strengths of the different types of construction. Due to secondary failures, such as leaks around the fittings, the possible strength of the tanks was not reached. In fact, the secondary failures were responsible for failure in each case. In one tank the failure was at the weld around a two-inch pipe outlet; in the second, at the manhole; in the third, at the end transverse weld, and in the riveted tank at the end transverse riveted joints. The first two failures might have been obviated by better welding of the pipe fittings and manhole saddle to the shell. Extra reinforcement at the junction of the spherical end to the cylindrical shell would have reduced the stresses at the junction where the other two tanks failed. The location of the end transverse seam or riveted joint farther back on the shell of the tank would have taken this joint out of the region of high stress intensity caused by the abrupt change in direction of force at the junction of the spherical end of radius four feet to the cylindrical shell of radius two feet.

As the results of the analysis of the deformation and distribution of stress in these tanks, the following general conclusions seem warranted:

1. The commonly accepted theory for the design of tanks is, for all practical purposes, sufficiently accurate, provided the computed stresses are not influenced by secondary stresses.

[4] Technologic Paper No. 243, price five cents.

2. For thin tanks, the measured stresses, based upon the two-dimensional formula, are in close agreement with the design stresses computed by the common-pressure formulas, provided the former are not affected by secondary causes. This is borne out by the results obtained at the centre of the end.

3. Secondary stresses resulting in high stress intensity were caused by (*a*) faulty design of the attachment of the spherical end to the cylindrical shell, (*b*) non-conformity of the shell to an accurate circular section, and (*c*) discontinuities in the shell for the manhole and fittings. These may produce a possibly dangerous condition if present near a welded or riveted joint or seam.

4. The stresses were increased by the presence of a seam.

UNITED STATES GOVERNMENT SPECIFICATION FOR WATER-RESISTING RED ENAMEL.[5]

THIS specification was prepared by the technical committee on paints of the Federal Specifications Board after careful consideration of suggestions from manufacturers. Highest quality red enamel suitable for outside use is called for. This consists of pure toluidine red toner in a vehicle of the very best water-resisting long oil spar varnish. A general description of the enamel is followed by detailed directions for sampling and testing, including tests for caking in container, working properties, color, hiding power, weight per gallon, coarse particles and skins, identification and determination of pigment, non-volatile matter, drying time, water resistance, and toughness.

UNITED STATES GOVERNMENT SPECIFICATION FOR GLOSS INTERIOR LITHOPONE PAINT, WHITE AND LIGHT TINTS.[6]

THIS specification was prepared by the technical committee on paints of the Federal Specifications Board after careful consideration of suggestions from paint manufacturers. Paints under this specification are not intended for outside exposure; they shall dry to gloss opaque coats that will adhere well to wood, metal and plaster, stand washing with soap and water, and show no material

[5] Circular No. 146, price five cents.

[6] Circular No. 147, price five cents.

change in color or exposure to light or material yellowing when kept in the dark.

A general description of the pigment, vehicle and completed paint, which is a lithopone zinc oxide pigment in a vehicle of treated drying oils or varnish, is followed by detailed directions for sampling and testing. The tests cover caking in container, color, weight per gallon, brushing properties, time of drying, resistance to washing, fastness to light, yellowing, determination of water, volatile thinner, percentage of pigment, percentage of non-volatile vehicle, nature of non-volatile vehicle, coarse particles and skins, and analysis of pigment.

Wetting of Glass and Quartz by Mercury. EARLE E. SCHUMACHER (*Jour. Am. Chem. Soc.*, 1923, **45**, 2255–2261) has attempted to cause mercury to wet glass and silica after removal of gases from the surface of the solid as completely as possible with present available means. Fairly good wetting was usually obtained in the case of quartz, but resulted only occasionally in the case of glass, becoming more difficult as the alkali content of the glass increased.

J. S. H.

Cupric Oxide Jellies. HARRY B. WEISER, of The Rice Institute (*Jour. Phys. Chem.*, 1923, **27**, 685–691), draws the following conclusions as the result of an experimental study of cupric oxide jellies. When a suitable concentration of colloid cupric oxide is precipitated at a suitable rate, a hydrous cupric oxide jelly is produced, for instance, ammonia is added to cupric acetate in the presence of a small amount of a sulphate, and the resulting colloidal solution is permitted to precipitate spontaneously. A colloid of suitable concentration does not result in the absence of sulphates. Jellies are not formed on the addition of ammonia to cupric sulphate, chloride, or nitrate, since a colloid is not formed, but a gelatinous precipitate is immediately deposited.

J. S. H.

Action of Silica on Electrolytes.—According to ALFRED FRANCIS JOSEPH and JOHN STANLEY HANCOCK, of the Wellcome Tropical Research Laboratories, Khartoum (*Jour. Chem. Soc.*, London, 1923, **123**, 2022–2025), silica reacts with an aqueous solution of sodium chloride to produce free acid and a complex silicate of low solubility, but alkaline reaction. It reacts in a similar manner with aqueous solutions of sodium sulphate, calcium sulphate, ammonium chloride, and calcium chloride. Experiments made with hydrochloric acid and with citric acid demonstrated that pure silica has no effect on the hydrogen-ion concentration of an aqueous solution of an acid.

J. S. H.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

CHEMISTRY OF THE KODACHROME BLEACH.[1]

By E. R. Bullock.

THIS paper is a discussion of the chemical reactions underlying the ozobrome and kodachrome processes. It is concluded that the bleach solutions act by converting the silver of the image into silver bromide, the potassium dichromate of the bleach being simultaneously partially reduced to chromic orthochromate, and the ferricyanide catalyzing this reaction. As regards the theory of catalysis in general, it is suggested that in certain instances at least an explanation may be based upon the assumption that the degree of simplicity of mechanism of a reaction is a factor in its velocity.

NOTE ON THE INFLUENCE OF CRYSTAL HABIT ON THE PHOTOCHEMICAL DECOMPOSITION IN SILVER BROMIDE CRYSTALS.[2]

By S. E. Sheppard and A. P. H. Trivelli.

IT is noted that while the visible photochemical decomposition has in common with the initiation of development the property of commencing at isolated points its further increase may be a relatively orderly process, orienting according to definite directions in the crystal. Although the growth of the photoproduct proceeds mainly by discontinuous increments, it is neither uniform, nor haphazard, but radiates along the lines of more rapid growth.

* Communicated by the Director.

[1] Communication No. 181 from the Research Laboratory of the Eastman Kodak Company and published in *B. J.*, Aug. 10, 1923, p. 491.

[2] Communication No. 182 from the Research Laboratory of the Eastman Kodak Company and published in *Phot. J.*, July, 1923, p. 334.

PREPARATION OF ALKYLGUANIDINES.[3]

By R. Phillips and H. T. Clarke.

METHYLGUANIDINE sulphate is formed in good yield from methyl iso-thiourea sulphate and methylamine in aqueous solution. Dimethylguanidine sulphate is also readily formed in the same way from dimethylamine. Methyl mercaptan is produced in the above reactions as a by-product. Its crystalline sodium salt is here described for the first time.

THE INTERFACIAL TENSION BETWEEN GELATIN SOLUTIONS AND TOLUENE.[4]

By S. E. Sheppard and S. S. Sweet.

THE relation of the orientation of specific atom groups in the molecule to the emulsoid state is discussed. Using ash-free gelatin, the separation of gelatin at a benzene-water interface was found to be affected by the presence of air. The stability of gelatin-air foam was found to be greatest at the iso-electric point. An investigation was made of the stability of gelatin-air foam as a function of hydrogen-ion concentration with the following results:

Temp.	30° Foam.	Half period.	40° Foam.	Half period.
p_H	c.c.	secs.	c.c.	secs.
1.29	40	45	25	30
3.80	40	50	25	45
4.34	40	75	30	90
4.58	40	150	30	120
4.78	40	180	35	150
4.82	60	180	40	180
4.87	70	300	35	180
5.00	70	300	40	180
5.10	70	300	40	150
5.20	50	300	35	90
5.39	40	240	30	60
7.60	40	150	25	60
10.30	35	90	30	45
12.20	40	60	30	30

[3] Communication No. 174 from the Research Laboratory of the Eastman Kodak Company and published in *J. Am. Chem. Soc.*, July, 1923, p. 1755.

[4] Communication No. 152 from the Research Laboratory of the Eastman Kodak Company and published in *J. Amer. Chem. Soc.*, Dec., 1922, p. 2797.

The interfacial tension between gelatin solutions of various hydrogen-ion concentration and toluene was measured at 30° C., 40° C., and 50° C. At the iso-electric point, the lowering of tension by gelatin increases rapidly. Secondary phenomena due to hydrolysis were observed.

SEPARATION OF XYLENES.[5]

By H. T. Clarke and E. R. Taylor.

A DESCRIPTION of a working method for the isolation of pure ortho, meta, and para xylenes from coal-tar. The meta isomer can be obtained in a technically pure state by fractional distillation; on treatment with hot dilute nitric acid, any ortho and para xylenes present are oxidized, and the pure meta compound is further purified by sulphonation with subsequent hydrolysis of the resulting sulphonic acid. The ortho and para xylenes cannot be obtained in nearly so high a state of purity as the meta; the preparation in pure form depends upon subjecting the appropriate fractions to selective sulphonation, followed by crystallization and selective hydrolysis of the sulphonated products. Para xylene is attacked more slowly than its isomers by concentrated sulphuric acid, and its sulphonic acid requires a higher temperature for its hydrolysis.

A PRELIMINARY STUDY OF THE PLUNGER TYPE OF JELLY-STRENGTH TESTER.[6]

By S. E. Sheppard and S. S. Sweet.

A NEW type plunger tester is described, with continuous chain increment loading and variable plunger heads. The effect of different shapes of plunger has been studied, and it is shown that a flat plunger, because the area of contact does not vary with the load, is the most satisfactory. Plungers with rounded base are unsatisfactory, producing load-deflection curves which are not straight lines. Using any diameter of plunger, the depth of jelly required should be at least 7 cm. Also, the ratio of the diameter of the plunger to the diameter of the vessel must be less than a certain value, or spurious jelly-strength values will be obtained.

[5] Communication No. 162 from the Research Laboratory of the Eastman Kodak Company and published in *J. Amer. Chem. Soc.*, March, 1923, p. 830.

[6] Communication No. 164 from the Research Laboratory of the Eastman Kodak Company and published in *J. Ind. Eng. Chem.*, June, 1923, p. 571.

This ratio of diameter of vessel to the diameter of plunger should be at least five. This plunger tester has been compared with the torsion type of instrument and a definite factor determined for converting jelly-strength into rigidities by the plunger method. This factor, the ratio between the rigidities as measured by the plunger method and the torsion machine, was found to be constant, using either ash-free or commercial gelatin. Jelly-strengths can be determined as accurately as viscosities and can be expressed in absolute units. The suggestion is offered that a standard type of plunger tester, with elimination of systematic errors, be agreed on by manufacturers and colloid chemists.

MODIFICATION OF THE SPENCE-KRAUSS-HERZBERG METHOD FOR MICROSCOPIC EXAMINATION OF PAPER PULP FIBRES.[1]

By E. P. Wightman.

A RAPID and simple technic for use in the visual comparison method of microscopically estimating paper pulp fibres is suggested. The method described below is believed to be time saving and to have improvements over the technic described by previous workers. A sample of paper, or pulp, to be examined is well pulped in the usual way. After the tube containing the sample has been shaken, a drop or two of the pulp is transferred to a clean microscopic slide by means of a pipette with exit of wide diameter. The fibres are teased apart and allowed to dry on the slide. After the slides of the whole series to be tested are completed as well as those of the standard pulps, containing known quantities by weight of the various kinds of fibres, the fibres on each slide are moistened with water and the excess removed. One reason for drying first, and then remoistening, is to allow the fibres to stick to the glass, otherwise it is difficult to be sure whether or not a representative sample remains on the slide. When the excess moisture has been removed Herzberg zinc chloride-iodine stain and a cover glass are added, and the excess stain is squeezed out. Preparation of all the samples in hand, as a whole, rather than carrying out the complete operation on each one separately, is advised.

[1] Communication No. 168 from the Research Laboratory of the Eastman Kodak Company and published in *Paper*, Feb. 14, 1923, p. 14.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

NEW SOURCES OF SANTONIN.[1]

By Arno Viehoever and Ruth G. Capen.

[ABSTRACT.]

OF the fifty-six species of domestic *Artemisia* studied in the Bureau of Chemistry, two (*Artemisia Mexicana* and *Artemisia neomexicana*) gave distinct tests for santonin. In a third (*Artemisia Wrightii*) the presence of santonin was indicated. Thus it would seem possible to utilize domestic plants, growing as weeds in barren fields, for making santonin.

FURFURAL FROM CORNCOBS.[2]

II—THE BUREAU OF CHEMISTRY EXPERIMENTAL PLANT AND PROCESS FOR FURFURAL PRODUCTION.

By Frederick B. LaForge and Gerald H. Mains.

[ABSTRACT.]

THE experimental plant in the Bureau of Chemistry used for the production of furfural from corncobs consists essentially of a pressure digester unit and a continuous column still. The cobs are digested with water and high-pressure steam, the vapors being condensed to form a dilute furfural solution which is concentrated in the column still.

Optimum operating conditions are: Pressure, 130 to 135 pounds (180° C.); ratio of water to cobs, 4 : 1; digestion period, two hours. The furfural yield obtained is 6 per cent. of the weight of cobs used. The column still separates from the dilute solution five to six pounds of crude (95 per cent.) furfural per hour with a 97 to 98 per cent. recovery. Small quantities of acetic acid, acetaldehyde, and methanol are by-products.

The process is simple and commercially feasible, and can be adapted to a number of agricultural wastes.

* Communicated by the Chief of the Bureau.

[1] Published in *J. Am. Chem. Soc.*, **45** (Aug., 1923) : 1941.

[2] Published in *Ind. Eng. Chem.*, **15** (Aug., 1923) : 823.

A REPORT ON SOME OF THE NON-GLYCERIDE CONSTITUENTS IN CRUDE COTTONSEED OIL.[3]

By George S. Jamieson and Walter F. Baughman.

[ABSTRACT.]

THE acetone (or petroleum ether) insoluble portion of the settlings, which constitutes 0.1 to 0.2 per cent. of the crude cottonseed oil, contains proteoses, peptones, resin, pentosans, raffinose, and inosite phosphates. The pentosans constituted 1.74 per cent. and the raffinose 4.2 per cent. of the acetone insoluble settlings. It was estimated that these settlings contained approximately 12 per cent. of inosite phosphoric acid. The presence of xanthophyll and a wax was indicated. Resin is the only constituent as yet isolated in appreciable quantities from that portion of the original settlings which was soluble in acetone. No protein, starch or tannin could be detected. Tests made indicated that gossypetin, quercetin, isoquercetin, and quercemeritrin were absent.

WEARING QUALITIES OF SHOE LEATHERS.[4]

By F. P. Veitch, R. W. Frey, and I. D. Clarke.

[ABSTRACT.]

THE results of a comprehensive study of the wearing qualities of leather conducted by the Bureau of Chemistry indicate that (1) retanned chrome and chrome-tanned upper leathers are superior in pliability to other leathers tested; (2) certain types of fibre soles have objectionable features, but that those which do not develop such features are very durable; (3) rolled vegetable-tanned sole leathers give approximately 16 per cent. longer wear than unrolled leathers of the same thickness; (4) loading sole leathers with glucose and Epsom salts does not materially affect their serviceability; (5) chrome-tanned sole leathers, especially unwaxed chrome-tanned leather, show a strikingly longer wear than the other kinds of sole leathers tested.

The experiments were conducted with army shoes and under exceptionally dry conditions of service, which points must be fully considered in connection with the results obtained. Particu-

[3] Published in *Cotton Oil Press.* **8** (Sept., 1923): 29.

[4] Issued as *U. S. Dept. Agr. Bul. 1168*, Sept. 5, 1923.

larly should this be borne in mind with regard to sole leather loaded with glucose and salts and with regard to unwaxed chrome-tanned sole leather. While the latter was the most serviceable in the tests described, it is generally known to be unsatisfactory for outdoor wear in humid climates because of the readiness with which water goes through it. Waxing overcomes this particular defect to a large extent.

Nitrates in the United States in 1922.—A report on the production and importation of nitrates during 1922 has been issued by the United States Geological Survey, the data having been prepared by G. R. MANSFIELD.

Sodium, potassium, and calcium nitrates are widely distributed in small quantities through many of the western and southwestern states. The most promising deposits, those of the Amargosa region, in southeastern California, were studied intensively by members of the United States Geological Survey during the war, and the results of these studies have recently been published. They showed clearly that these deposits, though interesting scientifically, were quantitatively insufficient for commercial development.

The Geological Survey still receives inquiries from time to time regarding nitrate deposits, but no evidence has yet been produced to show that in any of the deposits mentioned by correspondents the nitrate is of more than scientific interest. Although fine specimens or small lots of practically pure sodium and potassium nitrates have been found at many places the quantity has always proved insignificant.

No advance can be recorded in the production of atmospheric nitrogen in the United States for 1922. A comparatively small plant in New York State uses a modification of the Haber process, but its product is in a form not suitable for use as fertilizer. The United States Government has not yet disposed of the Muscle Shoals plant, but work has been resumed on the dam, which is the key feature of the project.

Chile Nitrate.—As reported by the Bureau of Foreign and Domestic Commerce, 149,570 long tons more of nitrates were imported into the United States from Chile in 1922 than in 1921, but the imports for 1922 were still far below the average over the last ten years.

Much of the material imported into the United States between 1914 and 1919 went to manufacturers of munitions. When the demand from this direction ceased, there were large stocks on hand in the United States and at the primary markets. As a result the total shipments to Europe, the United States, and to various other parts of the world dropped tremendously in 1919. In 1920 renewed confidence was evident, and exports from Chile to the United States and Europe tripled. By the end of that year this confidence had weakened, and in

1921 imports of nitrate in Europe and in this country were again greatly reduced. No proper basis has been established on which to estimate the consuming power of Europe and the United States, but it seems probable that for these countries it now exceeds that of the years prior to 1914.

Throughout 1922 considerable dissatisfaction was expressed at the manner in which sodium nitrate is handled in Chile, where a trust backed by the Chilean Government arbitrarily fixes its prices. Consumers contend that had the trust been willing to lower prices more nitrate would have been consumed throughout the world, but there is no evidence that the Chilean Government intends to change its present plan of operations.

Imports of Inorganic Nitrogen.—Sodium nitrate made up by far the greater portion of the imports of nitrogen compounds into the United States in 1922. Chile furnished practically all of this product. Calcium cyanamid, ammonium sulphate, calcium nitrate, and part of the sodium nitrate were imported for consumption in the fertilizer industry, the potassium nitrate and the remainder of the sodium nitrate for use in the chemical industries.

Atomic Weight of Antimony.—A preliminary study of the atomic weight of antimony derived from different sources has been made by SHEIKH D. MUZAFFAR, of Cambridge University, England (*Jour. Am. Chem. Soc.*, 1923, **45**, 2009–2013). Stibnite was obtained from Hungary, Borneo, Peru, and Bolivia; and each of the four ores was used separately for the isolation of pure antimony. The antimony had the following atomic weight according to its source: Hungary, 121.14; Borneo, 121.56; Peru, 121.72; Bolivia, 122.37. The striking variation in the value of the atomic weight suggests the presence of isotopes of antimony. J. S. H.

Further Tests upon Dewar Flasks Intended to Hold Liquid Air. H. BRIGGS and J. MALLINSON. (*Proc. Royal Soc., Edin.*, Vol. 43, Part 2.)—Metal flasks alone are considered. It is only when the necks are unusually short that the invasion of heat by conduction down the neck is of any importance. "With the long slender necks usually adopted for storage vessels that source of evaporative loss is either negligibly small or actually zero." The authors point out that improvements in the flasks are to be sought, not in the use of a higher vacuum between the inner and outer vessels, but in "greater attention to the polish of the reflecting surfaces, and to the means of preserving the lustre up to the time of evacuation." It is unwise to let a flask stand empty, for then the charcoal in the vacuum lets the adsorbed air pass away. This will tarnish the reflecting surfaces, thus making them better radiators. G. F. S.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting held Wednesday, October 17, 1923.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, October 17, 1923.

MR. CHARLES DAY, Vice-president, *in the Chair.*

The Board of Managers submitted their report. The report recorded the election of the following Resident Members:

William H. Balls, Esq.,
1422 Snyder Avenue,
Philadelphia, Pennsylvania.

Renshaw Borie, Esq.,
District Manager,
McClellan and Junkersfeld, Inc.,
Philadelphia, Pennsylvania.

Alexander Brown Coxe, Esq.,
Agriculturist,
Paoli, Pennsylvania.

Carleton Dean Haigis, Esq., D.Sc.,
Research Physicist,
Victor Talking Machine Company,
Camden, New Jersey.

Mrs. Selina Emma Peacock,
Organist,
Philadelphia, Pennsylvania.

Harold Pender, Esq., Ph.D.,
Dean, Moore School of Electrical Engineering,
University of Pennsylvania,
Philadelphia, Pennsylvania.

John Wagner, Esq.,
Philadelphia,
Pennsylvania.

Daniel Dorsey Wolf, Esq.,
Treasurer, C. C. Kampton and Sons, Inc.,
Philadelphia, Pennsylvania;

the following Non-resident Members:

W. G. H. Finch, Esq.,
Radio Editor and Engineer,
International News Service,
New York City, New York.

George F. Kunz, Esq., D.Sc., Ph.D.,
409 Fifth Avenue,
New York City, New York.

Israel Maizlish, Esq., Ph.D.,
Professor of Physics,
Lehigh University,
Bethlehem, Pennsylvania.

Alfred Oberle, Esq., Ph.D.,
Research Chemist,
Universal Oil Products Company,
Chicago, Illinois.

Archie Dayton Power, Esq., Ph.D.,
Professor of Physics,
University of Minnesota,
Minneapolis, Minnesota.

Richard H. Ranger, Esq., B.S.,
Radio Engineer,
66 Broad Street,
New York City, New York.

V. A. Suydam, Esq., B.S., Ph.D.,
Professor of Physics,
Beloit College,
Beloit, Wisconsin.

John Widmeyer, Esq., B.S.,
Metallographist,
Lancaster, Pennsylvania.

William Wilson, Esq., B.A., D.Sc.,
Engineer,
Western Electric Company,
New York City, New York;

and the following Associate Members:

Frank R. Garman, Esq., B.S.,
Engineering Assistant,
Bell Telephone Company,
Philadelphia, Pennsylvania.

Tobias Wagner, Esq.,
Philadelphia,
Pennsylvania;

and additions to the library by gift, 3529 volumes, 520 pamphlets and 1 drawing; by purchase, 94 volumes and 1 pamphlet, and by binding 298 volumes.

A report of progress was presented by the Committee on Science and the Arts.

The Chairman then announced that the next business of the meeting would be the presentation of the Elliot Cresson Medal to Raymond D. Johnson, for his invention of the "Johnson Hydraulic Valve," and recognized Mr. Benjamin

Franklin, Chairman of the Sub-committee of the Science and Arts Committee investigating the device.

Mr. Franklin said, "Mr. Chairman: The construction of large hydraulic and hydro-electric plants, involving either a high head or a large volume of water, has necessitated the design of a valve which would easily and safely control the flow of water.

"Mr. Raymond D. Johnson, the inventor of the Johnson Hydraulic Valve, has successfully solved this problem by employing the principle of the needle valve in controlling the flow of water in conduits under pressure perfecting a valve which is under complete control, either automatically, by hand, or by electrically operating at a distance, and which does not deform under operative strains. Valves of this type have been constructed which control the flow to a 37,500 H. P. hydraulic turbine, having a diameter at the inlet of twenty-one feet.

"The Sub-committee of the Committee of Science and Arts of The Franklin Institute, after a careful examination and a comparison with other types of valves at present commercially available, reached the conclusion that the Johnson Valve has the following notable characteristics:

(1) Great mechanical strength due to the cylindrical shape of all parts.
(2) Durability, as there are no sliding contacts under pressure and the plunger in operation is unbalanced only enough to move it.
(3) Tightness against leakage in the closed position.
(4) Powerful hydraulic operating forces within the valve to insure opening or closing under all conditions, without recourse to external sources of power.
(5) Simplicity of control, by hand or by electric means at a distance.
(6) Automatic closing feature which positively insures closing of the valve in case of a break below the valve, thus greatly reducing the danger of loss of life and property damage, which invariably follows such accidents.

"The report of the General Committee concludes as follows:

"'In consideration of the ingenuity and soundness of the design, excellence of construction and operating characteristics; successfully meeting the demands of commercial requirements, The Franklin Institute awards its Elliot Cresson Medal to Raymond D. Johnson, of New York, for his Hydraulic Valve.'"

The Chairman presented the medal and accompanying documents to Mr. Johnson, who thanked the Institute for the high honor conferred upon him.

The Chairman then introduced Dr. Arthur L. Day, Director of the Geophysical Laboratory and Chairman, Advisory Committee in Seismology, Carnegie Institution of Washington, who presented the paper of the evening on "Earthquakes and Volcanic Eruptions."

The speaker gave some of the results of the study of earth movements in California, obtained through accurate triangulation, for the determination of surface changes. He also gave a summary of the investigations conducted by the Carnegie Institution of Washington, of the destructive earthquakes in Chile, in November of last year, and by means of colored slides, illustrated the differences between the earth movements in California and in Chile. References

to volcanic phenomena were largely confined to recent eruptions of Etna, of which a number of colored slides were shown, portraying various stages of the several eruptions.

After a brief discussion a vote of thanks was extended to the speaker.

Adjourned.

R. B. OWENS,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(*Abstract of Proceedings of Stated Meeting held Wednesday, October 3, 1923.*)

HALL OF THE INSTITUTE,
PHILADELPHIA, October 3, 1923.

MR. W. H. FULWEILER, *in the Chair.*

The following reports were presented for final action:

No. 2800: Work of William Gaertner in the Design and Manufacture of Scientific Instruments. Howard N. Potts Medal to Mr. William Gaertner, of Chicago, Illinois.

No. 2808: Pneumercator. Edward Longstreth Medal to Mr. Harry S. Parks, of Philadelphia, Pennsylvania.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(*Stated Meeting, Board of Managers, October 10, 1923.*)

NON-RESIDENT MEMBERS.

DR. ALFRED OBERLE, Research Chemist, 343 South Oak Park Avenue, Oak Park, Illinois.

DR. GEORGE F. KUNZ, President, The American Scenic and Historic Preservation Society, Old Tribune Building, 154 Nassau Street, New York City, New York.

CHANGES OF ADDRESS.

MR. ROBERT ATKINSON, Box 153, New York University, University Heights, New York City, New York.

MR. J. SNOWDEN BELL, 149 Broadway, New York City, New York.

MR. C. O. BILLOW, 1431 Jarvis Avenue, Rogers Park, Chicago, Illinois.

MR. JOHN IRWIN BRIGHT, Devon, Pennsylvania.

JOSEPH H. BURROUGHS, Esquire, 612 Bullitt Building, Philadelphia, Pennsylvania.

MR. ERNEST H. DAVIS, 901 Vine Avenue, Williamsport, Pennsylvania.

MR. J. H. GRANBERRY, in care of American Can Company, Boston and Hudson Streets, Baltimore, Maryland.

MR. EDWARD W. HAMMER, 55 John Street, New York City, New York.

MR. WILLIAM H. HARDING, 1127 Land Title Building, Philadelphia, Pennsylvania.

MR. GEORGE E. KINNIER, 94 Broad Street, Woodbury, New Jersey.
MR. GEORGE MACLEAN, Port Washington, New York.
MR. T. C. MARTIN, 32 Grove Avenue, Larchmont Manor, New York.
MR. ALLEN I. MYERS, 565 West 113th Street, New York City, New York.
COLONEL SAMUEL REBER, Rochambeau Apartments, Washington, D. C.
MR. H. N. SPICER, 247 Park Avenue, New York City, New York.
MR. W. H. SUPPLEE, in care of The S. S. White Dental Manufacturing Company, Unity and Oakland Streets, Frankford, Philadelphia, Pennsylvania.
PROFESSOR V. A. SUYDAM, 1126 Porter Avenue, Beloit, Wisconsin.
MR. WILLIAM R. WEBSTER, 3818 Chestnut Street, Philadelphia, Pennsylvania.
MR. ROY V. WRIGHT, in care of Railway Age, 30 Church Street, New York City, New York.
MR. C. H. ZEHNDER, Room 3018, 120 Broadway, New York City, New York.

NECROLOGY.

Mr. E. G. Bashore, The Texas Company, Port Arthur, Texas.
Mr. H. W. Biddle, 424 Chestnut Street, Philadelphia, Pennsylvania.
Mr. Thomas De Witt Cuyler, Arcade Building, Philadelphia, Pennsylvania.
Mr. William J. Haines, 1011 Chestnut Street, Philadelphia, Pennsylvania.
Mr. Robert W. Hunt, 2200 Insurance Exchange Building, Chicago, Illinois.
Mr. A. Stein, 97 Gold Street, New York City, New York.

LIBRARY NOTES.

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BOOK REVIEWS.

LABORATORY DIRECTIONS IN INORGANIC CHEMISTRY. By Alexander Silverman, University of Pittsburgh. Second edition, revised. 56 pages, 4to. D. Van Nostrand Company, New York. Price, $1.25.

Works of this character are best employed by those who prepare them. Many such manuals are on the market, and each reflects to a dominant extent the method which the writer has adopted after considerable experience. It is usually unsatisfactory for a laboratory teacher to use any but his own manual. The book in hand has doubtless given satisfaction to large numbers of students,

and seems to be fully equal to the generality of works of its class. Herbert Spencer said that education does not form character, and his dictum finds application every day in the work of students in the elementary laboratory, for no amount of talking will secure universal care in managing apparatus. Bunsen burners will be allowed to have too much air, stoppers of bottles will be laid on dirty tables and many other minor sins committed against the principles of good chemistry. This book contains a large number of items of advice as to care and cleanliness. How far the teacher gets the student's obedience is not known. Minute examination of the book might show points on which instructors would differ, but in the main the data are correct and clearly expressed. In the preparation of oxygen with the mixture of potassium chlorate and manganese dioxide the quantity of the latter is as usual too large. Twenty-five per cent. of the dioxide is quite sufficient for the action. It is a question whether this catalyst may not be advantageously replaced by ferric oxide. The latter acts quite well in proportion of 25 per cent., and being bright red it cannot be confused with antimonous sulphide or charcoal, dangers to which the manganese compound is liable. Moreover a good grade of ferric oxide is now obtainable at a lower cost than a good grade of the manganese compound. It is evident that the book is intended to be used with a general textbook or with lecture notes. The illustrations deserve some animadversion. In common with those generally seen in elementary manuals, they are rather sketchy. The time has now arrived when the methods photo-engraving give, at moderate cost, excellent reproductions of actual apparatus, and the modern laboratory should no longer be supplied with makeshift materials. In this book, for example, the student is advised to put a stopper in the sink and use it for a pneumatic trough! Worse advice could hardly be given. HENRY LEFFMANN.

ALLOYS RESISTANT TO CORROSION: A summary of papers and discussions at a joint meeting of the Faraday Society and the Sheffield Section of the Institute of Metals. Pamphlet, reprinted from the *Transactions of the Faraday Society*, 8vo, 75 pages.

This pamphlet is filled with most interesting and valuable data. The corrosion of metals and alloys has great practical importance; any information concerning its causes and prevention is welcome to many branches of industry and to those interested in the household affairs. On the latter feature should be mentioned a report on a new silver alloy which does not tarnish. English standard silver is, as is well known, sterling, that is, only one-twelfth alloy (7½ per cent.). The British government will not "hall-mark" any other silver alloy. The new alloy is of this standard. In the preliminary report no statement is given as to the composition of the diluting metal, but, of course, this cannot be kept secret after the material comes into the market, though even then some special method of mixing may be held in confidence by the makers so that a monopoly may be maintained. The new alloy will be a great boon to those who delight in silver service at the table, for the manufacturer's agent reports that he has kept the ware in his house in use for two years without polishing. Considerable space is given to some of the iron alloys, such as the stainless steel and iron, which have become familiar in cutlery. Nickel-chromium alloys also receive attention. One paper is devoted to the "dry corrosion" of metals, that corrosion in which there is no direct contact with

water, but exposure to air. As might be expected, it is found that acid and alkaline vapors have marked action, sulphurous acid being dangerous to iron and nickel, ammonia to copper and hydrochloric acid to zinc and aluminum.

The pamphlet will well repay careful reading by all interested in practical use of metals and alloys.

HENRY LEFFMANN.

DISCOURS DE LA NATURE DE L'AIR, etc. Par Edma Mariotte. 118 pages, 12mo. Paris, Gauthier-Villars et Cie., 1923. Price, 3 Francs.

This is a volume of the series of reprints of the original communications of eminent French scientists of earlier days—Masters of Scientific Thought, is the specific title of the series. The name of Mariotte is indissolubly connected with physical chemistry, by reason of his discovery of the law of gas-pressure. Boyle shares with him, indeed, honor in this matter, but the preference has generally followed chauvenistic tendencies, for British writers almost always speak of Boyle's law and French writers of Mariotte's law. American writers are apt to avoid the issue, and speak of the law of Boyle and Mariotte. In accordance with French custom, the book has no index and a small "Table des Matières" at the back. A general statement is given of the object of the series and of the value of re-reading the works of the masters, then follows a biography of Mariotte, from which we learn that the data of his early life are somewhat scanty. He was born in Burgoyne about 1620 and lived a long while at Dijon, where he entered the church. In 1666 he was appointed as physicist at the Academy of Sciences, a position for which he was well qualified. This reprint of his works includes a discourse on the nature of the air, on the vegetation of plants and a "new discovery touching sight," which is an account of his discovery of the "blind spot" in the eye. These volumes are interesting reading, and seem to the reviewer to be especially suitable for students in chemistry and physics who have advanced in modern language study far enough to read French fairly well. The text is excellent and the story interesting and instructive.

HENRY LEFFMANN.

CHEMICAL CALCULATIONS. By R. Harman Ashley, Tufts College. xi–276 pages, 12mo. New York, D. Van Nostrand Company. Price, $3 net.

A work of this character that has reached a third edition needs little more than the announcement of its appearance. It is evident that it has met a wide acceptance and has been found satisfactory. A few errors are almost certain to creep into the first issue, but practical use by others than the author will soon detect these and they will be duly corrected. The work covers a wide field and enters into both elementary and advanced problems. Those who have large experience with students know how few are really ready with numbers. It is often astonishing how the student will go wrong on the simplest arithmetical calculation. In the present edition a great deal of attention has been given to logarithms, an addition that is very welcome in view of the increasing use of the logarithmic methods in chemistry and physics. The peculiar symbolism of hydrogen-ion concentration is very puzzling to anyone who has not a ready understanding of this method. The book is clearly printed, a matter of importance when figures are so largely used.

HENRY LEFFMANN.

YOUNGKEN'S PHARMACEUTICAL BOTANY. By H. W. Youngken, M.S., Ph.D., Professor of Botany, Pharmacognosy and Materia Medica, Massachusetts College of Pharmacy. Fourth edition, revised and enlarged, 63 illustrations and a glossary. xix–538 pages, 12mo. P. Blakiston's Son and Company, Philadelphia. Price, $4 net.

Professor Youngken's skill in laboratorium and scriptorium is so well known that any book by him will be recognized at once as competent. The present one, being a fourth edition, needs only the announcement of the publication. It contains in a compact form a large amount of information. The student of pharmacy is especially interested in botany. It is true that modern medicine has done away to a large extent with the use of the "simples that have virtue," and substituted concentrated and synthetic drugs, but enough still remains to need careful study. For such study, Doctor Youngken's book is eminently fitted. It is a manual of technic as well as of descriptive morphology, liberally illustrated with excellent drawings and photographs. As a preliminary to the study on pharmacognosy, it is highly commendable. The author, long known for his work in Philadelphia, has now gone to the "Hub," and will continue his original investigations and writings there. Boston's gain is Philadelphia's loss. HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 172, Dynamic Stability as Affected by the Longitudinal Moment of Inertia, by Edwin B. Wilson. 8 pages, quarto. Washington, Government Printing Office, 1923.

In a recent technical note (No. 115, October, 1922) of the Committee, Norton and Carroll have reported experiments showing that a relatively large (15 per cent.) increase in longitudinal moment of inertia made no noticeable difference in the stability of a standard S. E. 5A airplane. They point out that G. P. Thomson ("Applied Aeronautics," page 208) stated that an increase in longitudinal moment of inertia would decrease the stability. Neither he nor they make any theoretical forecast of the amount of decrease. Although it is difficult, on account of the complications of the theory of stability of the airplane, to make any accurate forecast, it may be worth while to attempt a discussion of the matter theoretically with reference to finding a rough quantitative estimate.

PUBLICATIONS RECEIVED.

A Textbook of Intermediate Physics, by H. Moore. 824 pages, illustrations, 8vo. New York, E. P. Dutton and Company, 1923. Price, $9.

The Elementary Principles of Lighting and Photometry, by John W. T. Walsh with a foreword by Sir J. E. Petavel. 220 pages, illustrations, 8vo. New York, E. P. Dutton and Company, 1922. Price, $4.50.

Advanced Practical Physics for Students, by B. L. Worsnop and H. T. Flint. 640 pages, illustrations, 8vo. New York, E. P. Dutton and Company, 1923. Price, $8.

Chemical Engineering Catalogue, 1923 (eighth annual) edition. 1056 pages, illustrations, quarto. New York, The Chemical Catalog Company, Inc. Leased at $2 per copy.

Chemical Calculations, by R. Harman Ashley. Third edition, revised. 276 pages, 12mo. New York, D. Van Nostrand Company, 1923. Price, $3 net.

Pharmaceutical Botany. A textbook for students of pharmacy and general science, by Heber W. Youngken. Fourth edition, revised and enlarged. 538 pages, illustrations, 12mo. Philadelphia, P. Blakiston's Son and Company, 1923. Price, $4.

Alloys Resistant to Corrosion. A general discussion held jointly by the Faraday Society and the Sheffield Section of the Institute of Metals, April, 1923. Reprinted from the *Transactions of the Faraday Society*, July, 1923. 75 pages, illustrations, 8vo. London, 1923. Price, 5 shillings 6 pence, net.

L'Idée de la Théorie de la Relativité, par H. Thirring. Traduit de l'Allemand par M. Solovine. 186 pages, illustrations, 12mo. Paris, Gauthier-Villars et Cie., 1923. Price, in paper, 8 Francs.

Laboratory Directions in Inorganic Chemistry, by Alexander Silverman. Second edition, revised. 55 pages, illustrations, quarto. New York, D. Van Nostrand Company, 1923. Price, $1.25 net.

Technical Books of 1922. A selection. 28 pages, 16mo. Brooklyn, New York, Pratt Institute Free Library, 1923.

National Advisory Committee for Aeronautics. Technical Notes, No. 153, Analysis of Dr. Schaffran's Propeller Model Tests, by Max M. Munk. 5 pages, diagrams, quarto. No. 157, An Impulse Motor for Driving Recording Instruments, by W. F. Joachim. 13 pages, illustrations, diagrams, photograph, quarto. No. 159, The Time Lag and Interval of Discharge with a Spring Actuated Fuel Injection Pump, by Robertson Matthews and A. W. Gardiner. 16 pages, diagram, quarto. No. 160, Fittings and Other Structural Parts of Airplanes, by P. Eydam. 12 pages, illustrations, quarto. Washington, Committee, 1923.

Engineering Education and American Industry. Special Report No. 25, National Industrial Conference Board. 25 pages, illustrations, 8vo. New York, Board, 1923.

Colors Shown by Rotating Discs When Illuminated by Two Sources of Light. A. STEICHEN. (*Physikal. Zeit.*, March 1, 1923.)—A disc with adjacent white and black portions is rotated. Let it be illuminated intermittently by light from an arc lamp that passes through holes in the periphery of another rotating disc so timed in speed that the first disc shall appear to be at rest. Then the black parts of the chief disc appear black while the white parts assume the color of the light from the arc. Now let a dim incandescent lamp shine upon the disc, so that it is lighted by a steady as well as by an intermittent source. The white parts of the disc take on a color similar to that of the arc light and the black portions appear to be of the complementary color, no matter what color be given to the light from the arc. This effect is connected with the formation of colored shadows. G. F. S.

A SERIES of demonstration experiments in the field of radioactivity is given in *Physikalische Zeitschrift*, March 15, 1923, by P. Ludwig, Freiberg, Saxony. G. F. S.

CURRENT TOPICS.

Investigations on X-rays by the Cloud Method. C. T. R. WILSON. (*Proc. Royal Soc.*, A724.)—The distinguished originator of this method of investigation returns to the experimental problem armed with all the skill that his long previous experience has given to him. Moist air is traversed by a beam of X-rays. From the atoms beta particles are ejected under the influence of the X-rays. These rapidly moving particles come into collision with atoms from which they set ions free. When the air is already supersaturated with water vapor by reason of having been suddenly expanded from its original volume, each ion becomes a nucleus for the condensation of a portion of the vapor. Thus the track of the beta particle becomes manifest through the succession of tiny drops condensed along its path. To bring about the needed actions three pendulums were released at the same time. The first at the lowest point of its swing opened communication between the moist air chamber and a vacuum, thus causing rapid expansion. The second sent a Leyden jar discharge through an X-ray tube from which a beam traversed the expanded air. The third sent a discharge through a mercury vapor tube, the light from which was used to photograph the tracks in the damp air. By the adjustment of sliding weights on these pendulums the operations were made to succeed one another at the proper interval.

Stereoscopic photographs were taken with two cameras having their axes at a suitable angle. "An inspection of the picture shows at once (1) the point of origin of each beta ray, (2) its initial direction (*i.e.*, the direction in which an electron has been ejected from its parent atom by the action of the radiation), (3) the total length of its path or range, (4) the form of the track, its sudden or gradual bends, and the number and direction of emission of any secondary beta rays (branches), and (5) the variation of the ionization along the track; under favorable conditions the number and distribution of the ions along the tracks may be obtained by direct counting."

The twenty-two figures appended are of remarkable clearness and beauty. It will be strange if the questions they have raised followed by the answers given do not greatly help in unravelling the process of the emission of a beta particle when a quantum of energy is absorbed from an X-ray. G. F. S.

Boundary Lubrication—the Latent Period and Mixtures of Two Lubricants. W. B. HARDY and IDA DOUBLEDAY. (*Proc. Royal Soc.*, A724.)—In general when a lubricant is applied to a solid surface the value of the friction diminishes as time passes until a steady condition is attained. The name "latent period" is given

to the time during which the diminution continues. "The latent period seems to be merely the time occupied in the orientation of the molecules of the lubricant at the solid face. The carbon chains of fatty acids, or alcohols, are loaded at one end with the –COOH or –OH groups, respectively. They may, therefore, be likened to rods loaded at one end. Placing a pool of fluid upon a surface is like flinging at it a handful of such rods grasped at random. Some will hit and stick by the loaded ends, others by the unloaded ends. The rods may be supposed to be attracted to the solid more strongly by their loaded ends, and the process of evaporation into the overlying fluid and condensation from it will increase the proportion of rods sticking to the solid face until a steady state is reached." "The proof that this view of the latent period is correct lies in one significant and striking fact, which seems to us to be open to no other interpretation. It is that molecules composed of a chain of carbon atoms, both ends of which are alike, do not manifest a latent period. Normal paraffins are such substances. In their case the rods are unloaded, and no matter how applied to the surfaces the first recorded value of the friction is the same as the last."

In the following data both plate and slider were of glass with heptoic acid as the lubricant. The latent period was forty-five minutes long, when a considerable amount of the acid was put on the plate and the slider was at once placed in it. The period lasted only ten minutes when both plate and slider were covered with lubricant, left in this condition for three hours and then brought together. When saturated vapor was passed for three hours into a chamber containing the plate and slider separated from each other, the latent period was five minutes in length after the slider was put upon the plate. In all these three cases the final value of the coefficient of friction came out the same. Temperature has a marked effect on the length of the latent period. For one set of conditions it had the values 45, 15 and 5 minutes at the temperatures 15°, 48° and 72° C., respectively. Stirring a pool of lubricant on the plate with the slider likewise shortens the latent period. G. F. S.

Airplane-bombing Tests on Battleships.—Much interest was awakened some months ago by the newspaper accounts of the sinking of the battleships *Virginia* and *New Jersey* by bombs dropped by airplanes. Many considered the results as indicating that the battleship is wholly out of date, but others held that the attack on undefended vessels was no positive trial of the method. The U. S. Air Service has now issued a pamphlet containing authentic reports of the methods and results of these tests, being a complete transcript of the address of Major-General Mason M. Patrick, Chief of the Air Service, on September 13th last, before the Military Order of the Veterans of the World War at Washington. The address began by a quotation from the writings of Francesco Lana, who, in 1670, expressed the possibility that aircraft could be the means of destroying cities and ships. General Patrick then traced the developments

within recent years, alluding briefly to Zalinski's dynamite gun, which he stated was a failure, and to the efforts of the Germans to utilize dirigibles in attacks on cities. In the attacks on London and Paris a good deal of damage was done, but no attempts seem to have been made to attack ordinary war vessels, although a few were made on submarines. After the war, the army and navy of the United States took up the problem of the possible destruction of war vessels by airplanes. The first experiments were on two German ships that had been surrendered to the United States on condition that they would be destroyed and on the *Alabama*. These ships were destroyed and the tests were regarded by many as showing no battleship so far constructed was safe against well-operated airplanes. The Air Service does not, however, declare the battleship obsolete. The following paragraphs are from the report of General Patrick's address:

"Only a few days before the actual tests, the War Department directed that the first bombing should be done at a height of not less than 10,000 feet. We did it, but there is no other air service organization in the world that could have done the same thing. We sent our planes not to 10,000 feet, but to 11,200 feet, each of them carrying more than 2000 pounds of bombs. To do this we had to use superchargers. When a man climbs to a considerable height he finds difficulty in breathing. The percentage of oxygen in the air is less and without artificial aid he cannot exercise his full power. A motor acts in precisely the same way. The Liberty motor gives about 400 H. P. at sea level. In the rarer air at considerable distances above the earth this power falls off rapidly. The supercharger, in simple terms, is merely an air-pump which condenses this rarer air and feeds it into the motor at sea level density, thus the power of the motor can be sustained. By the way, it was with such a supercharged motor that Macready attained a height of nearly seven miles, an altitude record which stood for some time, although I believe that a Frenchman has just bettered it by a few feet."

"The first attack was made at a height of over 10,000 feet. The planes with their loaded bombs left Langley Field early in the morning, each carrying four 600-pound bombs. They flew about 170 miles, passed through three rainstorms, came out over the *New Jersey*, released their projectiles, and of the twenty which were launched, not less than four from this great height made direct hits upon the vessel's deck. That was exceedingly good practice. The two attacks upon the *New Jersey* were followed by an attack with 1100-pound bombs upon the *Virginia*. One of these struck square on the deck. The three funnels and two masts were swept away and much other damage was done. It is scarcely conceivable that any personnel on the deck would have been left alive. Almost immediately after this hit a bomb fell close alongside and inflected a fatal blow. Just six minutes and thirty-five seconds after that particular bomb left the airplane the *Virginia* disappeared beneath the waves."

"Another thing to be remembered is that conditions for this bombing were exceedingly favorable. We knew precisely where the

boats were anchored, the sea was perfectly calm, the visibility excellent. Of course, there was no opposing fire from the vessels. As a matter of fact, the Air Service does not greatly fear anti-aircraft fire from ships. There will almost always be some motion of the vessels to interfere with the accuracy of such fire and we believe that at best its effect will be to keep the airplanes somewhat higher.

"Furthermore, even though we have losses, and in war such must be expected, we are satisfied that the damage we can do will more than offset them. Again, it may be stated with confidence that the defense against an air attack is an opposing air force. The navy hereafter must rely upon aircraft with the fleet to protect it from hostile airplanes. To provide for our national defense we must then have an adequate air force. Airplanes that scout far out to sea could from their height readily detect the approach of a hostile expedition. Remember that at a height of 5000 feet the visible horizon is 100 miles away. At 10,000 feet it is 150 miles away and the air-man from this elevation sees over a water area of about 60,000 square miles. Remember, too, that the speed of the airplane is from four to five times as great as the ordinary speed of vessels. If a hostile fleet is discovered from 200 to 300 miles off shore, the aircraft can report its presence by radio or can return to its base and give warning. Normally it would take such a fleet ten to fifteen hours to reach the vicinity of its attack. In one-half that time, from properly chosen concentration points, an air force could be assembled to meet the coming attack." H. L.

Earthquake Records and Tidal Waves. (U. S. Department of Agriculture, Clip Sheet No. 277, October 15, 1923.)—While seismological or earthquake records can not be used directly in predicting quakes, they have other practical uses. When these records are collected and studied they throw a great deal of light on the nature of earthquakes generally, and it is conceivable that at some future time this information may lead to successful methods of prediction.

In one way, however, which is illustrated in the practice of the Hawaiian Volcano Observatory, conducted by the Weather Bureau of the United States Department of Agriculture, seismological records are of immediate practical utility. Severe earthquakes within oceanic areas frequently are attended by so-called tidal waves. There may be an interval of many hours between the occurrence of the quake and the arrival of the destructive oceanic wave at any given place. When a violent earthquake appearing to have occurred in the Pacific Ocean is registered at the Hawaiian observatory, the officials send out warnings by cable or otherwise to the regions likely to be affected by the accompanying tidal waves, so that the people may not be caught unprepared. This service is said to have resulted in a great saving of life and property.

Carbon Dioxide as a Refrigerant. J. H. PRATT (*Ice and Refrig.*, 1923, **65**, 141–143) has made a study of carbon dioxide as a refrigerant and draws the following conclusions: "Briefly summing up the advantages and disadvantages of carbon dioxide, as compared with other refrigerants, it is generally believed that its use will become more and more popular, as the great advantage of safety, coupled with the fact that the operating efficiency is practically as good as other mediums, more than overcomes the imaginery difficulties with the higher pressures, particularly when operated in northern climates with ordinary cooling water temperatures." J. S. H.

New Indicators.—BARNETT COHEN, of the Hygienic Laboratory, U. S. Public Health Service (*Pub. Health Reports*, 1923, **38**, 199), describes five new indicators of the sulphonephthalein series. Meta cresol purple (*m*-cresol sulphonephthalein) changes from red to yellow in the P_H range 0.5 to 2.5, and from yellow to purple in the P_H range 7.6 to 9.2. Brom-chlor phenol blue (Dibromodichlorophenol sulphonephthalein) changes from yellow to blue in the P_H range 3.2 to 4.8. Brom cresol green (Tetrabromo-*m*-cresol sulphonephthalein) changes from yellow to blue-green in the P_H range 4.0 to 5.6. Chlor phenol red (dichlorophenol sulphonephthalein) changes from yellow to red in the P_H range 5.0 to 6.6. Brom phenol red (dibromophenol sulphonephthalein) changes from yellow to red in the P_H range 5.4 to 7.0. J. S. H.

AT INTERVALS there is issued a yellow paper-covered volume of the *Proceedings of the Royal Institution of Great Britain*. It is safe to say that no other group of a few hundred pages contains so much thoroughly up-to-date scientific information in so delectable a form. The most recent number contains a report of the lectures delivered at the Royal Institution in 1920. In the first Sir Charles Parsons tells how a temperature of more than 15,250° C. was obtained and outlines a method of producing a pressure, instantaneous to be sure, of 7000 tons per square inch. Under the caption "Problems of Lubrication," W. B. Hardy makes this statement: "If a glass vessel, such as a bottle, be placed upon an inclined pane of glass at a certain angle, it slips smoothly down. The glass plate is an ordinary plate cleaned with a cloth. In the usual sense of the word the surface of the plate is not lubricated, the surface is 'dry.' The lower half of the plate is then wetted with water and the bottle is now found to slip on the unwetted part, and to be sharply pulled up by friction when it reaches the wetted part. It is not sufficient, therefore, to interpose a liquid film between solid faces to get lubrication. . . . Here is another plate picked up at random in the laboratory of the Royal Institution. Its composition is unknown. Tested in the same way, water has no detectable influence on the friction between the glass and the surface of the plate. It will be well to confess at once that these simple experiments raise questions which are as yet without an answer." "Low

Temperature Studies," Sir James Dewar; "The Gyrostatic Compass," S. G. Brown; "The Scientific Work of the Late Lord Rayleigh," Sir J. J. Thomson; "Crystal Structure," W. L. Bragg; "The Thermionic Valve in Wireless Telegraphy," J. A. Fleming; "Blue Sky and the Optical Properties of Air," Lord Rayleigh; "The Menace of Man's Dispersal of Insect Pests," H. M. Lefroy—all these find a place. Less rigidly scientific, but not less interesting, is the lecture on "String Figures" the string figures we all held on our hands years ago, wherein we learn that there is a whole book on the subject. Edward McCurdy presents Leonardo da Vinci as a rare combination of the artist, the scientist and the technician. And how modern was he! "He contemplated the use of poisonous gas or powders in naval warfare for the purpose of suffocating the enemy, and told how to make a simple preventive mask. He also contemplated the contingency—as happened on occasions in Flanders—of an adverse wind causing the poison to recoil upon the users." G. F. S.

Short Sound Waves. KONSTANTIN PALAIOLOGOS. (*Zeit. f. Physik.*, Jan. 9, 1923.)—Following the plan of Martens the sound waves were obtained from a direct current arc on which was superimposed a weaker alternating current. The resulting current never fell to zero but possessed a series of maxima to each of which there was a corresponding maximum of gas pressure. In this way the arc sent out a succession of condensations. The lengths of the emitted waves were measured by means of an acoustical grating and for these experiments ranged from 1.71 to .17 mm. Every time that a sound wave was emitted there was at the same instant an electrical wave started, the length of which was found from a wave meter. The two kinds of waves, the electrical and the acoustical, have the same frequency and the lengths of both were determined as already stated. The velocities would then be in proportion to the respective wave-lengths, and since the velocity of the electric wave is known, the velocity of the sound wave can be calculated. When this was done it appeared that no change in velocity could be detected for a change in wave-length from .17 mm. to ten times as much.

G. F. S.

Atmospheric Dust. (Clip Sheet, U. S. Department of Agriculture, No. 274.)—Visibility is a large factor in air flight and in various surface operations, especially navigation. A knowledge of conditions governing visibility is therefore of considerable importance. Dustiness or mistiness may be due to incomplete combustion of coal or other fuels, seen as smoke at lower levels. Some dust particles come from volcanoes. Some, it is thought, may come from interplanetary spaces.

The Weather Bureau of the United States Department of Agriculture was provided with an instrument for measuring atmospheric dust, known as a dust counter, by the section of meteorology of the

International Union of Geodesy and Geophysics in Rome, in May, 1922. A dust count has been taken daily during the past year by the Weather Bureau from the surface at Washington, D. C., and from the top of the Washington Monument. The War Department has also permitted aviators at Bolling Field to coöperate with the Weather Bureau, taking tests at different levels, from 1000 feet to 10,000 feet above ground.

The dust counter used collects the dust from a known volume of air and deposits it on a small and very thin glass disc, where by means of a powerful microscope the particles can be counted and their character determined. Tests have shown about 90 dust particles per cubic centimetre on a very clear, dry day and as high as 933 per cubic centimetre on one day of limited visibility, but with the same dry condition of the air which prevailed on the former occasion.

R.

Anomalous Magnetic Permeability of Nickel and Steel Wires in Weak Alternating Fields of High Frequency. B. WWEDENSKY and K. THEODORTSCHIK. (*Physikal. Zeit.*, May 15, 1923.)—Wires of 15 cm. length and of a few hundredths mm. in diameter were subjected to the fields of rapidly alternating currents of wave-lengths ranging from 54 to 585 m. The permeability of both nickel and steel varies in a complicated way with the wave-length employed. Steel shows no less than three maxima. The lowest permeability found for nickel was 8.5 and the highest 18.2 for wave-lengths of 54 and 585 m., respectively. For the sample of steel used the corresponding values are 32.5 and 72 for wave-lengths of 54 and 187 m. "The variation of the permeability with wave-length indicates the presence of a selective absorption or magnetic conductivity."

G. F. S.

Pilot Balloon Work. (Clip Sheet, U. S. Department of Agriculture, No. 274.)—Pilot balloon observations are now conducted by the Weather Bureau of the United States Department of Agriculture at one additional station at Memphis, Tennessee. They are telegraphed to Chicago and Washington. Original records of the observations are later mailed to the central office for reduction and study.

The eastern half of the country is fairly well covered, with the addition of this station and with those operated by the Army and Navy. West of the Great Plains, however, there is an extensive area almost entirely without free air data.

Through coöperation with authorities of the Dutch West Indies, pilot balloon observations are being made at Curacao during the hurricane season. It is possible that arrangements can be made later to have them taken throughout the year. Much of the instrumental equipment has been furnished by the Weather Bureau, which receives in return data by radio or cable. These observations, with those at

San Juan and Key West, furnish information of value in connection with the formation and movement of hurricanes.

Another example of mutually helpful coöperation in pilot balloon work is the furnishing of equipment, through the department of terrestrial magnetism of the Carnegie Institution, to the Apia Observatory, Samoan Islands. In this case also copies of the observations are forwarded to the Weather Bureau for study. R.

Kilauea Volcano Observatory. (Clip Sheet U. S. Department of Agriculture No. 278, October 22, 1923.)—A field of activity of the Weather Bureau of the United States Department of Agriculture that is but little known is the volcano investigations conducted on the island of Hawaii under Dr. T. A. Jaggar, Jr. The permanent scientific staff consists of a volcanologist, a seismologist, and a chemist. Occasionally chemists, geologists, seismologists, and physicists, both from the United States and from foreign countries, spend from a few weeks to several months at the Volcano Observatory.

The observatory is situated about 4000 feet above sea level on the brink of Kilauea Volcano, which is continually active, with a lake of molten lava. Studies are made not only of that volcano but also of Mauna Loa, nearly 10,000 feet higher, which erupts every five or six years. The eruptions of the two volcanoes are not explosive but take the form of a rather quiet extrusion of molten lava.

The routine of the station consists in daily observation and photography of the fire pit, frequent surveys to determine the height of the lava, care of several seismographs, and interpretation of seismograms. The seismograms give the distance and direction of earthquakes—five or six occur each week—and indicate the amount of tumescence or subsidence of the entire mountain top. From these seismographic data forecasts of volcanic activity from two or three hours to several days in advance are often made.

The Measurement of Thermal Conductivity. E. GRIFFITHS and G. W. C. KAYE. (*Proc. Royal Soc.*, A 724.)—A knowledge of thermal conductivity is essential in the designing of electrical machinery and of refrigerating and heating plants. For the measurement of this physical constant in substances of low conductivity, these two workers in the National Physical Laboratory have devised three pieces of apparatus with the especial purpose of economizing both time and effort. Against the face of a copper block heated electrically is put a thin plate of the substance under investigation. Heat from the copper flows through the plate into a second copper block kept cool by a stream of water circulating about it in a copper worm. The heat developed in the coil warming the first block is calculated from the resistance and the current strength. The heat removed through the worm is got by the method of the continuous flow calorimeter. One would surely expect the former of the two authors to employ

the results of his valuable experience in this method. Thus the heat supplied to the plate, as well as the heat given up by it, were measured, a check on accuracy being thereby furnished. "With proper precautions the agreement reached 1 per cent. or less." One apparatus was made for slightly compressible materials, such as pasteboard and hard wood, easily procurable in discs 45 mm. in diameter and from .5 to 4 mm. in thickness. The degree of excellence in the contact between the test material and the copper blocks was examined by varying the pressure and measuring the coefficient of conductivity. Changing the pressure from 23.2 to 61.1 pounds per square inch made no certain difference. Indeed an increase of pressure sometimes made the coefficient greater and sometimes less, thus indicating that the contact was not a factor in the measurement. "Probably the most searching test that can be applied to the apparatus, particularly as regards the thermal contact at the bounding surfaces, is the comparison of results obtained when samples of the same material in different thicknesses are tested." This test was made with three specimens of walnut. The thicknesses were .06, .09 and .15 cm., respectively. The corresponding coefficients came out .000326, .000328 and .000324 in c.g.s. units.

Apparatus No. 2 "was designed primarily for those materials of which the contact resistance at the hot and cold plates is high and for which the use of amalgamated plates becomes necessary. The same apparatus proved also to be convenient for the study of variation from point to point in the conductivity over the area of a large sheet of material, such as ebonite or micanite." For the amalgamation to assure good contact, it was found that the plates must be fairly flat. Of course a correction was applied for the fall of temperature through the mercury film.

Apparatus No. 3 was for materials obtainable in thin layers only, so that a considerable quantity of heat traversed the layers and had to be provided by the heating coil.

The effect of moisture content on conductivity was investigated in the case of spruce. As the content rose from 3.4 per cent. to 17.0 per cent. the conductivity rose linearly from .000292 to .000340.

The coarser the grain of wood, *i.e.*, the fewer the annual rings per inch, the smaller is the conductivity. The conductivity parallel to the grain is about twice that perpendicular to the grain and either radial or tangential to the rings. The radial conductivity is about 5 or 10 per cent. larger than the tangential, since in travelling tangentially the heat meets the interstices between the fibres as well as the medullary rays, whereas the rays do not interfere with the passage of the heat radially.

Silk fabric, rice paper and Balsa wood all have a coefficient of approximately .0001. No other wood showed as small a value as the last named, which has a density of only 6 or 9 pounds per cubic foot.

G. F. S.

The Thermal Conductivities of Metal Crystals—I. Bismuth. G. W. C. KAYE and J. K. ROBERTS. (*Proc. Royal Soc.*, A 724.)—Hitherto all the measurements of the thermal conductivity of metals have been made upon pieces of metal containing the crystals in random arrangement. The purpose of this investigation is to determine the conductivity of a metallic crystal in different directions with regard to the crystalline axis and to compare the values thus obtained with the conductivity of an ordinary piece of the same metal. Bismuth was chosen because large crystals can be grown and because it does not crystallize in the cubic system.

Parallel to the trigonal axis the conductivity was found to be in c.g.s. units .0159. Perpendicular to the axis it is .0221. The ratio of the conductivities is 1.39. This ratio had been measured by others and ranged from 1.37 to 1.49.

On the assumption that ordinary bismuth is a conglomerate of small crystals, its conductivity should be .0195. Jaeger and Diesselhorst have obtained by measurement the value .0193, which is sufficiently near to the computed value. G. F. S.

The Sensitivity of the Ear as a Function of Pitch. F. W. KRANZ. (*Phys. Rev.*, July, 1923.)—"The sensitivity of the ear can best be expressed in terms of the minimum sound intensity which is audible." The source of sound was a thermophone. In this the alternating current from a vacuum tube oscillator flows through a platinum strip supported in the case of a telephone receiver held firmly against the observer's ear. The periodic changes of temperature in the metal cause corresponding changes in the pressure of the confined air, from which the sensation of sound arises.

By varying the inductance and capacity of the oscillating circuit it was possible to get a range of frequencies from 360 to 3000 per second. The procedure was the following: The intensity was fixed at so small an amount that it was insufficient to produce even the least sound at any frequency. The intensity was then doubled and kept constant while the range of frequencies was run through. At certain frequencies the constant intensity barely produced the sensation of sound. These frequencies were noted. The intensity was thereupon doubled and again the range of frequencies was tried. At frequencies different from those previously noted sound was heard. The increase in intensity was made a sufficient number of times.

Thirty normal ears were examined. In one instance a certain intensity was just great enough to be audible at no less than seven frequencies or pitches. It was quite common to find five such frequencies. The right and the left ears of the same person are not alike and the difference is at times astonishingly great. In one particular case one ear required at a frequency of 1600 per second about 100 times as much intensity for audibility as did the other ear. In still another ear lowering the frequency by 80 cycles, little more than

a semitone in the part of the scale concerned caused the sensitivity to become 200 times as great.

From person to person the curves connecting intensity and sensitivity vary to such an extent that it would seem that they might be used, as are the Bertillon prints, for purposes of identification, were it not necessary to have the untramelled judgment of the observer in order to form the curve. From the average results of the thirty ears examined, it is evident that the sensitivity increases from a frequency of 360 up to that of 1500. Over the range from 1500 to 3000 there is little change. G. F. S.

A New Method of Getting Residual Rays (Reststrahlen). M. CZERNY. (*Zeit. f. Phys.*, Vol. 16, July, 1923.)—In 1896 Rubens and E. F. Nichols published a method of separating from the entire complex of infra-red radiation a limited range of wave-lengths, the residual rays. This consisted in causing the complex to be reflected in turn from a series of polished, flat plates of a non-metallic substance such as rock salt that shows in the infra-red a marked metallic reflection. Those wave-lengths for which the reflector acts as a polished metal emerge from the last reflection but little weakened, while the other wave-lengths, for which the reflecting plates are transparent, come out materially reduced in strength. A drawback of the method lies in the need of finding a different reflector for each particular group of wave-lengths and, further, of getting from three to five large plates of it polished.

The ordinary sources of radiation for work in the infra-red emit very little energy in waves shorter than .0005 mm. By far the largest quantity of energy is given off in waves whose lengths range from .0005 to .012 mm. (radiation of short wave-length). It is the gamut of waves extending from the last up to those about a dozen times as long, from wave-length .012 mm. to .150 mm., for which the residual ray method is especially applicable. For this range there is considerable energy present, but it falls off rapidly with increasing length of wave. There is only a little energy in all the waves together whose lengths exceed .150 mm. The problem of segregating the residual rays depends upon discovering some way of reflecting the infra-red radiation in such a manner that the radiation of short wave-length be enormously reduced, while at the same time the residual rays are not greatly weakened. The author finds his solution in following a suggestion made by Rubens that the angle of polarization be employed. First, the complex of infra-red radiation is plane polarized by reflection at the proper angle from selenium mirrors. The reflected light then falls on a plane mirror of a substance having metallic reflection of the residual rays. The angle of incidence is determined by calculation so that there shall be no reflection at all of the plane polarized light whose wave-length places it in the middle of the radiation of short wave-length. Thus the reflected light is weak in wave-lengths both longer and shorter than the one that is extinguished, but retains

in considerable strength the longer wave-lengths that are metallically reflected. In spite of the loss they have suffered in becoming plane polarized the residual rays come out of the new process approximately as strong as in the former method. This loss is avoidable by the use of rock salt or fluorspar instead of the selenium plate. Selenium is largely free of dispersion and consequently plane polarizes a wide range of wave-lengths, while the other substances mentioned reflect the infra-red radiation with the short wave-lengths polarized and with the long waves of residual radiation not polarized. When this mixture of light in different conditions falls on the second plate at the proper angle, it is still the short waves that are extinguished. The residual rays are reflected without being polarized.

The fundamental idea of the method is, as has been said, due to Rubens, and according to the author is "probably the last suggestion made by him in the long series of methods which he devised for the isolation of infra-red waves." He died in July, 1922. G. F. S.

In Crystals is Sliding Friction Independent of the Pressure Normal to the Surfaces? M. POLANYI and E. SCHMIDT. (*Zeit. f. Phys.*, Vol. 16, July, 1923.)—Inside of a steel cylinder a weight was supported on bearings so that it would move parallel to the axis of the cylinder, when this was tilted. From the weight a rod ran to the end of a wire firmly supported at the other end. When the cylinder was tilted, the weight pulled on the wire and tended to stretch it. The wire was a single crystal of tin or of zinc produced by Czochralski's method. The yielding of the wire took place along planes determined by its crystallographic constants. Did the force required to make one plane slide over its neighbor depend on the pressure at the planes? To find the answer the cylinder was inclined until the wire, seen through a protected window, just began to lengthen. It was at once replaced in its first position, the pressure within was raised by means of a CO_2 cylinder and the experiment was repeated. It was impossible to find any difference of angle caused by a change of the pressure from 1 to 40 atmospheres, and yet in the latter case the surfaces must have been pressed together with forty times as much force as in the former, since the pressure within the cylinder was applied equally in all directions. G. F. S.

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